

EXERCISES IN GAS ANALYSIS

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TRANSLATED FROM THE FIRST GERMAN
EDITION (WITH CORRECTIONS AND
ADDITIONS BY THE AUTHOR)

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GAS ANALYSIS

PART I

The Analysis of Gases

Ex. 1.—To measure a definite volume of air in the Hempel burette.

The Hempel gas burette (fig 1) consists of two tubes, A and B, each mounted on a heavy iron foot, and having side tubes, *a* and *b*, which are joined by a long piece of thick-walled rubber tubing *c*. The tube A is the measuring tube, and is calibrated to 100 cu. cm, each cubic centimetre being again subdivided into $\frac{1}{2}$ cu. cm. The calibration begins just above the iron foot, and the tube is etched in such a way that the figures, counting from the bottom, read from 0–100 on the one side and from 100–0 on the other. The tube B is not calibrated, and is known as the levelling tube. The measuring tube ends in a short length of glass capillary tubing, to which a piece of thick-walled black rubber tubing *d* is firmly attached by a ligature. In order to measure a definite volume of air (100 cu. cm.) at the prevailing temperature and pressure, by means of this apparatus, distilled water at room temperature is first poured into the levelling tube, until both tubes are about half full. On pouring in the water, air bubbles are often trapped in the connecting tubing *c*, and these may easily, in the course of an

analysis, find their way into the measuring tube, and so vitiate the result. In order, therefore, to remove any air bubbles which may be present, the tube *c* must be squeezed between the thumb and forefinger, commencing at either *a* or *b* and continuing along to the opposite end. When all the air is removed the tubing *d* is closed with a pinchcock, which should be placed as near to the end of the glass capillary as possible.

The levelling tube is now raised with the left hand and the pinchcock opened with the right, until the water completely fills the measuring tube and begins to overflow through *d*, when the pinchcock is closed. The whole apparatus from the end of the tube *d* to the surface of the levelling tube is now completely filled with water, and is ready to receive the gas to be measured.

The levelling tube, after pouring away the greater portion of the water it contains, is then placed on the floor, and the pinchcock cautiously opened. Air streams into the measuring tube, displacing the water into the levelling tube. Rather more than 100 cu. cm

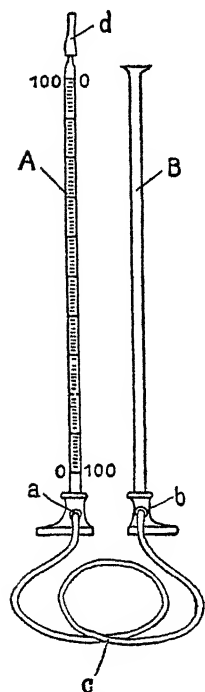


Fig 1

should be allowed to enter, the pinchcock then closed, and the levelling tube placed on the bench

The apparatus is now allowed to remain at rest for about 5 min. (the time being preferably measured by a sandglass), to allow time for the liquid adhering to the walls of the tube to collect together and run to the bottom.

If the reading is taken immediately, and the volume adjusted to 100 cu cm without allowing time for the liquid adhering to the sides to collect together, this liquid will subsequently run to the bottom, and the volume actually measured will be less than 100 cu cm (see Ex 2)

In order to measure exactly 100 cu cm. of air at the prevailing temperature and pressure the eye is brought to the level of the 0 or 100 mark, and the tube *c* compressed between the fingers in the neighbourhood of *a* until the liquid stands exactly at the 100 mark. The measuring tube now contains exactly 100 cu cm of air at the prevailing temperature, but under a pressure greater than atmospheric pressure. To correct this over-pressure the pinchcock is opened for a moment, the tube *c* being kept closed. The excess of air thus escapes, and the gas now stands under the required conditions of temperature and pressure. To confirm this, the burette is held by the iron supports, care being taken not to touch the measuring tube with the hands, so that the lower edges of the meniscus in measuring and leveling tubes are exactly level and the whole raised to the level of the eye. The lower edge of the meniscus in the measuring tube should then stand exactly at the 100 mark, if this is not the case the experiment must be repeated. In a similar way 50, 75, &c., cu cm. of air should be measured.

If the measuring tube be touched with the hands the enclosed gas will be warmed, and its volume will be consequently increased. According to Gay-Lussac's law, all gases expand $\frac{1}{273}$ of their volume at 0° for each 1° rise in temperature.

If 100 cu cm of air are enclosed in the measuring tube, and this be warmed only 1° by contact with the hands, the resulting error will amount to nearly 0.3 per cent by volume.

If a gas other than air is to be measured, the tube *d* is attached to the source of this gas, which is allowed to stream into the measuring tube. The subsequent procedure is then exactly as described above.

Ex. 2.—To determine the amount of error introduced by not allowing the liquid over which the gas is measured sufficient time to collect.

The measuring tube of a Hempel burette is completely filled with water, as described in Ex 1, and as much water as possible poured out of the levelling tube. The latter is then placed on the ground, and about 85–95 cu cm of air allowed to stream into the measuring tube by opening the pinchcock.

The burette is then grasped by the iron stands, the level of the liquid in the two tubes adjusted to the same height when held at the level of the eye, and the volume of air read off as quickly as possible. After recording the volume the apparatus is allowed to remain quietly for 5 min. (using sandglass), and the volume of gas read off again in precisely the same way. It will be observed that between the two readings there is a difference which may even amount to as much as 1 cu. cm. Before, therefore, reading off the volume of a gas in any measuring vessel, sufficient time must be given to allow of the liquid, over which the gas is measured, to collect on the walls and run down the sides of the tube, otherwise erroneous results will be obtained.

With aqueous liquids 5 min is usually sufficient, but if the liquid be strongly alkaline then a longer time must be allowed, as strong solutions of caustic soda or potash, being less mobile, require longer to run together and flow down the walls. If mercury, however, is the liquid there is no necessity to wait, as this substance has no tendency to adhere to the glass walls of the tube.

Ex. 3.—Determination of the amount of oxygen in the air by means of the Hempel burette and an alkaline solution of pyrogallol.

Exactly 100 cu. cm. of air are first measured in a

Hempel burette. The levelling tube is then placed on the ground level, the rubber tubing compressed tightly near to the end of the levelling tube, and as much water as possible poured away. Care must be taken that sufficient liquid remains to seal the end of the side tube.

The absorption reagent is now prepared by mixing together in a small flask 15 cu. cm. of an aqueous solution of pyrogallol (5 g pyrogallol + 15 cu. cm water) and 50 cu. cm. 60-per-cent caustic potash solution. This mixture is then poured into the levelling tube. In order now to bring this reagent into contact with the air enclosed in the measuring tube the burette is grasped by the iron feet, and the levelling and measuring tubes alternately raised and lowered as far as the length of the rubber tubing joining them will allow. In this way the reagent is gradually transferred to the measuring tube, which is recognizable from the colour of the solution.

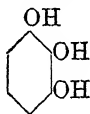
When a quantity of reagent has thus been brought into the measuring tube this is lowered as much as possible, the levelling tube remaining on the bench, and the connecting tubing closed by a clip as near to the end of the former as possible. The point of the measuring tube is now raised and lowered several times, so that the reagent flows up and down the tube, wetting the walls of the tube thoroughly, and coming into intimate contact with the gas. The oxygen is gradually absorbed, and the pressure in the tube falls. On opening the clip on the connecting tube, therefore, a further amount of reagent enters, and this is also brought into intimate contact with the gas in the manner described.

This operation is continued until the whole of the oxygen is apparently absorbed. The apparatus is then allowed to remain at rest for at least 5 min., and the volume read off in the usual way. The reagent is again

brought into intimate contact with the gas by inclining the tube for some time, and after waiting again for 5 min. the volume is again read off. The first and second readings should agree exactly, otherwise the operation must be repeated, until the volume of the gas shows no further diminution, after thoroughly shaking with the reagent. The difference between the original volume and the volume of the residual gas gives the volume of oxygen which has been absorbed. As the original volume of air taken was exactly 100 cu. cm, the difference gives the oxygen content of the air direct in percentage by volume.

Result—This should not be less than 20.2, or greater than 20.4 per cent oxygen by volume.

The pyrogallol used for absorbing oxygen is a white crystalline substance readily soluble in water. Chemically it is 1, 2, 3 tri-hydroxy-benzene.



An aqueous solution of pyrogallol is not able to absorb oxygen until an alkali has been added, when oxygen is greedily absorbed. Pyrogallol dissolves in a perfectly air-free solution of caustic potash giving a colourless solution, but if a trace of oxygen be present the solution becomes violet and ultimately an intense brownish-black. This reaction may be used to detect traces of oxygen. Potash which has been purified by means of alcohol cannot be used in the preparation of alkaline pyrogallol, as Hempel has proved that this always gives wrong results. The absorption of oxygen by alkaline pyrogallol is greatly influenced by temperature, which should never be lower than 17°. At 7° the reagent is distinctly less active. The chemical reactions which are

involved in the absorption of oxygen by an alkaline solution of pyrogallol are even yet completely unknown.

• **Ex. 4.**—Estimation of carbon dioxide in a mixture of carbon dioxide and air, using the Hempel burette.

The absorption liquid used in this experiment is an aqueous solution of caustic potash. 20–30 cu. cm of carbon dioxide, obtained from a Kipps' apparatus, are measured in a Hempel burette over water which has previously been saturated with this gas.

As carbon dioxide is distinctly soluble in water, it is necessary to measure it over carbon dioxide water, i.e. over water which has been previously saturated with the gas. If distilled water were used, the gas would be continuously dissolved, so that no exact measurement would be possible.

To bring the gas into the burette a piece of rubber tubing attached to a short length of glass tubing with a right-angle bend is connected to the delivery tube of a Kipps' apparatus.

The gas is allowed to stream through this for a short time to displace air, and then the other end of the glass tube, whilst the gas is slowly issuing, is slipped into the end rubber connection of the burette, which together with the burette itself has previously been completely filled with carbon dioxide water. By opening the pinch-cock the required amount of carbon dioxide is allowed to stream into the burette. The tap of the gas generator is then closed, and the delivery tubes removed. After waiting 5 min. the volume of gas in the measuring tube is read off.

As much water as possible is then poured out of the levelling tube, and this placed on the ground level. The pinchcock is then cautiously opened, and air drawn into the burette until the 100 mark is nearly reached. After waiting 5 min. the total volume is read off.

A further quantity of water is now poured out of the levelling tube, and replaced by the absorption reagent (40 cu. cm. dilute potash solution), and this is brought into intimate contact with the gas mixture exactly as described in the previous exercise.

Example —

Volume of CO ₂ measured	23.4 cu. cm.
Total volume	96.8 "
After absorption with KOH	73.6 "
CO ₂ found = 96.8 — 73.6	23.2 "
Error	0.2 "

The absorption of carbon dioxide by caustic potash takes place much more rapidly than the absorption of oxygen by alkaline pyrogallol. When sufficient reagent has been transferred to the measuring tube, it is only necessary to incline the tube up and down three or four times to ensure complete absorption.

Ex. 5.—To prove that an error is introduced by measuring carbon dioxide over water which has not previously been saturated with this gas.

About 20 cu cm of carbon dioxide are first measured accurately in a Hempel burette over distilled water. The connecting tube is then closed by compressing between the fingers, as close to the measuring tube as possible, and the gas brought into intimate contact with the liquid by raising and lowering the point of the burette several times. After standing for some time the volume of gas is again read off, when a considerable diminution in volume will be observed. If the gas and liquid be shaken together sufficiently long, the carbon dioxide will almost completely disappear. It is obvious from this experiment that if carbon dioxide, or gases containing carbon dioxide, are to be measured, the liquid over which they are confined must first be saturated

with carbon dioxide. If large quantities of a gas mixture to be analysed are available, it is best to measure the gas over water previously saturated with it.

What has been said of carbon dioxide holds equally good for other gases or mixtures of gases, e.g. acetylene or coal gas, which are more or less soluble in water. An experiment which is the reverse of the one here illustrated is described in Ex. 9.

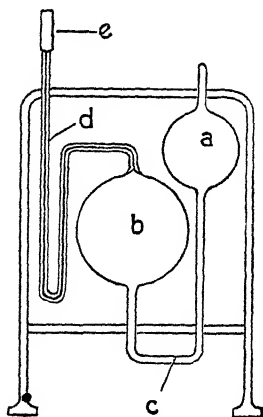


Fig 2

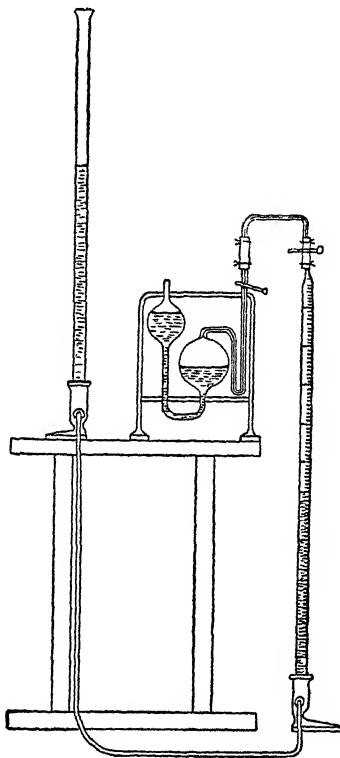


Fig 3

Ex. 6.—To transfer 100 cu. cm. of air from the Hempel burette to the Hempel gas pipette, and to return it to the burette.

The *Hempel gas pipette* consists of two glass bulbs *a* and *b* (fig. 2), which are connected by a bent tube *c*. The bulb *a* holds about 100 cu. cm. and *b* about 150

cu cm. A capillary tube d with several bends is fused on to b , and a short piece of thick-walled rubber tubing is attached to the end of this. The whole apparatus is mounted on a wooden or iron stand.

To carry out the experiment 100 cu cm of air are first accurately measured over distilled water in a Hempel burette. The gas pipette is then filled with water, and the rubber end tube closed by a pinchcock as near to the end of the capillary tube as possible. A capillary connection tube is then inserted into the rubber

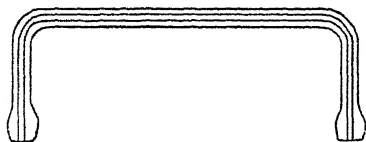


Fig 4

tube, and firmly fastened with a ligature of wet twine.

The capillary connection consists of a glass capillary tube bent twice at right angles, and having the ends

thickened somewhat, so that they may not readily slip out of the rubber tubes in which they are to be inserted (fig 4).

A quantity of air will be enclosed in the capillary tube d of the pipette and in the capillary connection, and this requires to be removed. To do this the pinchcock is opened, and the pipette held obliquely with the capillary underneath. Water will then siphon over and displace the air in the tube. A few drops of water are allowed to fall to ensure that all air is displaced, the pinchcock closed, and the pipette returned to its original position. If there should, however, be a large air bubble in the bulb b , this cannot be removed completely in this manner. It must be removed by opening the pinchcock, and blowing into the bulb a until all air is removed. It is necessary to observe very carefully that no air bubbles remain in the capillary, and when this is really the case the pipette is ready to be connected with the burette. Before, however, inserting the

glass capillary connection into it, the rubber endpiece of the burette must first be completely filled with water. This is done by inserting a little bent glass pipette filled with water as far as possible into the rubber tube

The little pipette (fig 5) consists of a short piece of glass tubing drawn out to a fine point and bent at right angles. It is advisable always to keep the pipette in a dish of water or dilute acetic acid, so that it is ready for immediate use

It is not advisable to fill the tube by blowing in water from a wash-bottle, as this is liable to cause air bubbles to be entangled.

After filling the end tube with water, the burette is stood upon a low stool, and the pipette upon the table, so that the tubes which are to be connected may be at

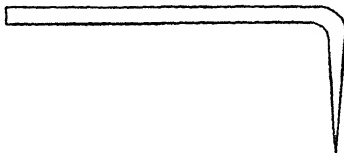


Fig 5

the same level. This can easily be adjusted by means of wooden blocks. The capillary connection of the pipette is then pushed into the tubing of the burette as far as possible, and the connection made secure with a wet ligature (fig 3). The levelling tube is now completely filled with water, the pinchcock of the pipette released so that it hangs loosely on the stand, and the levelling tube raised high with the left hand, at the same time opening the pinchcock of the burette with the right hand. The measured quantity of air in the burette is thus forced over into the pipette, the pinchcock being kept open until water just begins to enter the pipette, which now contains the 100 cu. cm. of air measured. To return the air to the burette the levelling tube is placed on the ground, and the pinchcock of the burette opened until the air has been drawn back again and water begins to enter the burette, after completely filling the connections. The pinchcock of the pipette

is now closed, so that when the latter is disconnected the capillary tube remains filled with water. The ligature on the burette is then removed, and the capillary connection withdrawn. After waiting 5 min the volume of air in the burette is again read off. The volume should still be exactly 100 cu. cm, otherwise the exercise must be repeated.

Ex. 7.—Determination of the amount of oxygen in atmospheric air by means of the Hempel burette and pyrogallol pipette.

The pyrogallol pipette (fig. 6) used in this experiment

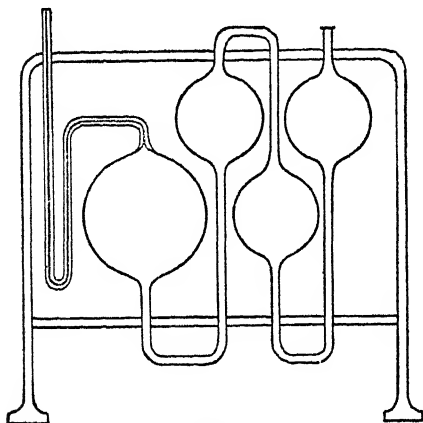


Fig 6

is really a double Hempel pipette. It consists of the simple Hempel pipette, to which a second pair of bulbs has been fused. These, like the first, are filled with an alkaline solution of pyrogallol, and serve the purpose of protecting the absorption reagent in the first bulbs from the

action of the oxygen of the air. Such compound pipettes are always used when the reagent is easily affected by atmospheric oxygen. To carry out the determination 100 cu. cm. of air are first measured accurately in a Hempel burette over distilled water. The burette is then connected with the absorption pipette exactly as described in the previous exercise, the air transferred into the pipette, and the pinchcock of the

burette closed. If the pipette be allowed to stand quietly, absorption of oxygen will slowly take place. To accelerate the rate of absorption the air must be brought into intimate contact with the reagent. To do this the top of the burette is held by the left hand, and the pipette by the right hand, and the latter shaken vigorously for about 5 min. (*Use sandglass*). The residual gas is then returned to the burette, and the latter disconnected. After waiting for 5 min the volume of gas is read off. The burette must now be again connected with the absorption pipette, the gas transferred to it, vigorously agitated with the reagent for another minute, and then returned to the burette. The volume is again read off, and should agree with the volume first read off. If this is not the case, the gas must be again shaken in the pipette.

Result should be 20.4 to 20.7 per cent oxygen.

In all cases when a gas constituent is absorbed in the Hempel pipette it is advisable to shake the gas twice with the reagent, reading off the volume of unabsorbed gas after each shaking. Only in this way can one be quite certain that the absorption is quite complete. A second shaking may, however, be dispensed with in the case of the potash pipette, as carbon dioxide is exceedingly readily absorbed by caustic potash.

The reagent used in the pipette is prepared by mixing a solution of 5 g. pyrogallol in 15 cu. cm. water with 120 g. caustic potash dissolved in 80 cu. cm. water, the solutions being preferably mixed in the pipette itself. According to *Hempel* such a solution has an absorption value of 2 to $2\frac{1}{4}$, i.e. 1 cu. cm. of this solution will absorb with certainty 2 to $2\frac{1}{4}$ cu. cm. oxygen. The analysis of a gas mixture by the aid of both burette and pipette has the advantage over the burette alone that the gas is always measured over the same liquid. It can readily be proved that the volume of a gas is not only dependent on temperature and barometric pressure, but also on the

nature of the liquid over which the gas is measured. The volume of a gas measured over a liquid is always greater than the volume of the same weight of gas, under the same conditions of temperature and barometric pressure but absolutely dry. This increase of volume is dependent on the vapour pressure, or tension of the liquid over which the gas is measured. The tension of a liquid depends upon its chemical composition, and also upon the temperature, but is independent of the barometric pressure. If, for instance, the volume of a quantity of gas be measured over water, and then over a saturated solution of calcium chloride, the volume will be smaller in the second case than in the first, owing to the fact that a saturated solution of calcium chloride has a much smaller vapour tension than water has.

If a constituent of a gas mixture be measured with the Hempel burette alone, an error due to tension is introduced. For example, in the estimation of the amount of oxygen in air by means of alkaline pyrogallol, the original volume of air is measured over water, whilst the volume of the residual gas is measured over a strongly alkaline solution of pyrogallol. These two liquids have, however, quite different vapour tensions, and an error is therefore introduced. The same error also occurs in the estimation of carbon dioxide in a mixture of carbon dioxide and air, using a solution of caustic potash in the Hempel burette.

If, therefore, comparable results are to be obtained the gas must always be measured over the same liquid, and this is readily done by using the Hempel pipette in combination with the Hempel burette.

Ex. 8.—Estimation of carbon dioxide and oxygen in a mixture of carbon dioxide and air.

Carbon dioxide is absorbed in a pipette containing a

solution of caustic potash. This may either be a simple Hempel pipette, or better, a Hempel pipette arranged to hold both solids and liquids. Such a pipette (fig 7) is similarly constructed to an ordinary Hempel pipette, but has one bulb replaced by a cylindrical vessel provided with a tubulure. To use such a pipette as a potash pipette the cylinder is first packed full of little rolls of iron wire gauze, these being introduced through the tubulure. The caustic potash solution is then poured in, and the tubulure tightly closed with a rubber stopper secured with string. Such a potash pipette has the great advantage over an ordinary pipette that on passing in the gas containing CO_2 , a considerable amount of absorption liquid remains entangled among the meshes of the wire gauze, thus increasing the absorbing surface enormously. As a consequence carbon dioxide is absorbed so rapidly that it is quite unnecessary to shake the pipette.

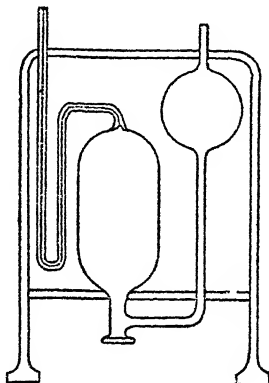


Fig 7

To carry out the experiment a mixture of carbon dioxide and air is prepared in a Hempel burette over carbon dioxide water, as described in Ex 4. The burette is then connected with the potash pipette, and the gas mixture forced over. After waiting a few seconds for the absorption of carbon dioxide to take place the gas is returned to the burette, and after standing 5 min. the volume of residual gas is read off. It is advisable, before returning the gas, which is now free from CO_2 , to the burette, to replace the carbon dioxide water in the latter by distilled water, to avoid the danger of carbon

dioxide diffusing out of the liquid into the gas, and so introducing an error (*See next exercise*)

To change the water in the burette after the gas has been transferred to the pipette, the pinchcock of the latter is closed, the ligature loosened, and the capillary connection withdrawn from the rubber tube. The whole of the water is emptied out of the burette and replaced by distilled water, the measuring tube and capillary connection being quite filled. The rubber joint of the pipette is then filled with water, using the small bent pipette, the capillary connection inserted and secured with a ligature, and the gas then returned to the burette.

After the volume of carbon dioxide absorbed has been read off and noted, the burette is connected with a pyrogallol pipette, the gas transferred to it, and the oxygen absorbed. The unabsorbable gas residue is then returned to the burette, and after waiting the necessary time, the volume is read off. The gas is again brought into the pyrogallol pipette and shaken with the reagent, then returned to the burette and measured.

The first and second readings should agree

Example.—

Volume of CO ₂ measured	=	25.4 cu. cm	
Total volume	=	98.6	„
∴ Volume of air	=	98.6 — 25.4 = 73.2	„
Volume of oxygen in air taken (73.2 cu. cm)	=	15.3	„
Volume after absorption with KOH	=	73.4	„
∴ CO ₂	=	98.6 — 73.4 = 25.2	„
Volume after absorption with pyrogallol	=	58.4	„
∴ O	=	73.4 — 58.4 = 15.0	„

The result is then calculated into percentages by volume.

Composition of Gas Mixture		Found
25.8 per cent CO ₂	.. .	25.6 per cent CO ₂
15.5 per cent O	15.2 per cent O

The caustic potash solution used in filling the potash pipette is prepared by dissolving 1 part of caustic potash in 2 parts distilled water. Such a solution has an absorption value of at least 40.

Besides the advantage already mentioned (avoidance of errors due to vapour tension), working with the burette and pipette together has the further advantage over working with the burette alone that more than one constituent of a gas mixture can be estimated by using different absorption pipettes.

If a gas mixture is to be analysed with the burette and a series of pipettes, *it is absolutely essential that these pipettes should be used in a definite order.* In analysing a mixture of carbon dioxide and air as just described, for example, it is not allowable to absorb the oxygen first with alkaline pyrogallol, for then this alkaline solution would also dissolve carbon dioxide, and the result obtained would be of no value.

Ex. 9.—To prove that an error is introduced by measuring a gas free from carbon dioxide over water saturated with that gas.

About 50 cu. cm. of air are first measured accurately over water saturated with carbon dioxide. The gas is then brought into intimate contact with the liquid by depressing and raising the point of the measuring tube several times. After waiting the usual 5 min. the volume of gas is read off, when it will be found to have undergone a decided increase.

This proves that if air or any gas free from carbon dioxide be measured over carbon dioxide water, an exact result cannot be obtained, the volume being always increased by carbon dioxide which diffuses out of solution.

What is true for carbon dioxide water also holds good

for water saturated with any other readily soluble gas. It is therefore always necessary in the course of a gas analysis, as soon as the readily soluble gas constituents are removed, to change the liquid over which they were measured. This is especially true when working with the *Bunte* burette, which is later described.

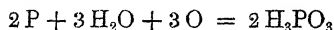
Ex. 10.—Determination of the amount of oxygen in the air by means of the phosphorus pipette.

The phosphorus pipette consists of a simple Hempel pipette for solid and liquid substances, the cylindrical part of which is filled with thin sticks of yellow phosphorus immersed in distilled water.

100 cu cm of air are measured in a burette, this then connected with the phosphorus pipette and the gas transferred. It is often not possible to transfer the whole 100 cu cm at one time to the pipette, owing to the amount of room occupied by the solid phosphorus. In this case part of the gas is transferred over, followed by the remainder as the oxygen is absorbed. Very soon after the air comes in contact with the phosphorus white fumes are noticeable, the oxidation of the phosphorus begins, and the oxygen disappears. The removal of the oxygen is observable in the falling of the water level in the second bulb of the pipette. When the fumes begin to die away, the absorption of oxygen is complete. This usually requires about 5 min at ordinary temperatures. When absorption is complete the residual gas is returned to the burette, and after waiting the necessary 5 min. the volume is read off. On returning the gas to the burette it is usually noticeable that the white fumes are also carried over. These, however, exert such a slight tension as to cause no appreciable difference in the result. The result should show 20.5 to 20.7 per cent O.

Phosphorus is converted by oxygen in presence of

water into phosphorous acid, the reaction being represented by the equation



According to this equation, 1 g. of phosphorus requires 0.77 g. = 538 cu cm of oxygen to convert it into phosphorous acid. The absorption value of phosphorus is thus very high, and as the oxidation product is readily soluble in water, the surface of the phosphorus is continually being renewed, enabling many analyses to be made with it. The phosphorus pipette has the advantage over the pyrogallol pipette, not only of much greater absorption value, but also in not requiring to be vigorously shaken, as is always essential with the latter. This very elegant method of absorbing oxygen by means of elementary phosphorus is, however, greatly limited by certain peculiarities which this substance possesses.

There are a considerable number of substances which, even when present in only very small amount, prevent the action of oxygen on phosphorus. Such substances include phosphoretted hydrogen, sulphuretted hydrogen, carbon bisulphide, chlorine, bromine, iodine, nitrogen peroxide, ethylene, acetylene, ether, alcohol, petroleum, oil of turpentine, and creosote. The presence of $\frac{1}{1000}$ volume of phosphoretted hydrogen, $\frac{1}{100}$ volume ethylene, or $\frac{1}{111}$ volume of turpentine vapour in the gas to be analysed will entirely prevent the absorption of oxygen by phosphorus. Owing to this peculiarity the use of the phosphorus pipette in many gas analyses is quite inadmissible. Phosphorus has, too, another peculiarity. If the partial pressure of oxygen in a gas mixture be high, i.e. if the gas contain a high percentage of oxygen, no oxidation of the phosphorus takes place, phosphorus is in fact not attacked by pure oxygen at temperatures below 23° C.

If, however, oxygen be diluted with 25 per cent of an indifferent gas, combination takes place with explosive violence. In order that the reaction may proceed quietly, not more than 50 per cent of oxygen must be present in the gas. If a gas mixture containing a higher percentage than this of oxygen is to be analysed in the phosphorus pipette, it must first be diluted with a sufficient quantity of an inert gas. The analysis of commercial oxygen may, for example, be made with the phosphorus pipette by proceeding in the following manner — About 80 cu cm of air are roughly measured in a Hempel burette, and the oxygen contained in this amount removed by absorption in the phosphorus pipette. The residual gas, consisting of about 64 cu cm of nitrogen, is measured accurately in the burette, and a known volume of the oxygen to be tested added. This gas mixture is now analysed in the phosphorus pipette.

The rapidity of absorption of oxygen by phosphorus, like the absorption by alkaline pyrogallol, is dependent on the temperature. Absorption proceeds normally at about 20° C, at 14° about $\frac{1}{4}$ hr is necessary for complete absorption, and at 10° as long as $\frac{1}{2}$ hr. The phosphorus pipette should always be kept in a dark place, or else protected from the action of light by covering with a cardboard box.

This is necessary because yellow phosphorus when exposed to light soon becomes covered with a layer of the red modification, which is unable to absorb oxygen at ordinary temperatures. This layer protects the yellow phosphorus from the action of oxygen, and renders it useless.

Ex. II.—Determination of the amount of oxygen in electrolytic detonating gas, using an alkaline solution of sodium hyposulphite in the *Pfeiffer* gas pipette.

The *Pfeffer* gas pipette (fig. 8) consists of two glass bulbs, A and B, each of a capacity of about 150 cu. cm. These are connected by a bent glass tube c. Attached to the bulb B is a short capillary tube a, to which are fused a glass tap b, the construction of which is readily understood from the diagram, and a thistle funnel c. To facilitate handling, the lower portion of the pipette is embedded in plaster of paris in a wooden box.

To prepare the apparatus for use an alkaline solution of sodium hyposulphite is poured in, then a piece of thick-walled rubber tubing, in which is inserted a

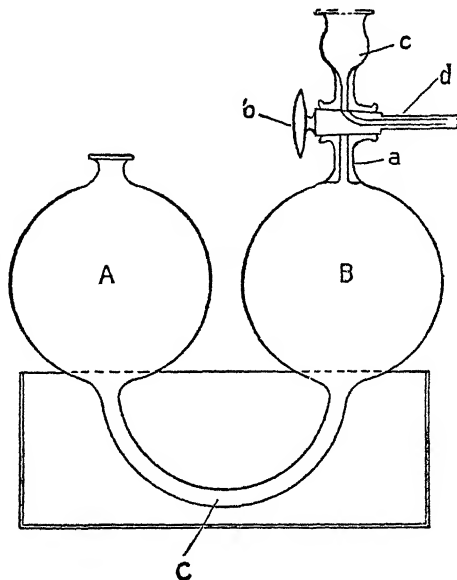


Fig 8

capillary connection with one right-angle bend only, is attached to d. By blowing into the bulb A, and suitably turning the tap, the whole of the air can be displaced from B and from the tap and capillary tubes. The tap is then closed.

100 cu. cm. of electrolytic detonating gas, obtained from a Hempel electrolytic generator, are measured accurately in a burette, the latter then connected with the pipette and the gas transferred over. The tap is then closed, the burette disconnected, and the gas

vigorously shaken with the reagent in the pipette. When the absorption is complete the bore of the tap and capillary connection are filled with water from the funnel *c*

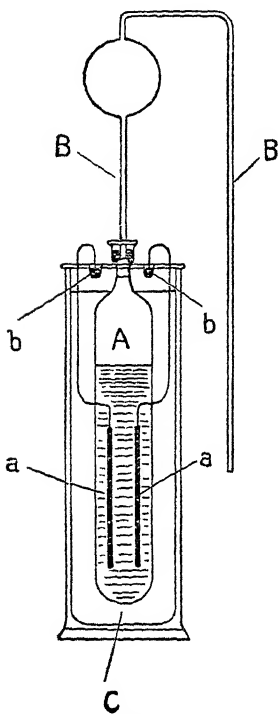


Fig 9

by suitably turning the tap, the burette connected, the gas transferred back, and the volume read off.

Result: — 33.0 to 33.2 per cent O.

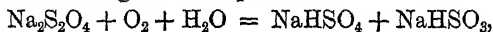
The Hempel detonating-gas generator (fig. 9) consists of a glass vessel *A* filled with dilute caustic potash, into which two platinum electrodes *a, a* are fused. A bent tube *B* provided with a bulb of about 50 cu. cm. capacity is ground into the neck of *A*. This vessel, the actual gas generator, is enclosed for safety in the outer vessel *C*, being held securely by a large cork. The wires attached to the electrodes dip into two small cups *b, b* filled with mercury, let into this cork, which serve to join up the apparatus to a source of electricity.

The reagent used for filling the pipette is prepared by mixing a solution of 50 g. commercial sodium hyposulphite dissolved in 250 cu. cm. water

with 40 cu. cm. of concentrated caustic soda solution (500 g. NaOH in 700 cu. cm. water).

The sodium hyposulphite employed is not the sodium "hyposulphite" used in photography, the correct chemical name for which is sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. (Translator)

The reaction between sodium hyposulphite and oxygen proceeds according to the equation



the sodium hyposulphite taking up one molecule of oxygen, and being converted into a mixture of sodium hydrogen sulphate and sodium bisulphite. The absorption value of this reagent is considerable, 1 g. sodium hyposulphite being able to absorb about 128 cu cm oxygen.

Compared with the absorption reagents already used, viz alkaline pyrogallol and phosphorus, alkaline hyposulphite offers many advantages. Compared with alkaline pyrogallol it has the advantages of being much cleaner to work with, has a greater absorption value, and is much cheaper, whilst it is superior to the phosphorus pipette in being unaffected by the substances which prevent the oxidation of phosphorus by oxygen. Over both reagents it has the very great advantage that the rate of absorption is quite independent of the temperature at which the reagent is used. Using an alkaline solution of sodium hyposulphite it is immaterial whether the absorption is carried out at 20° or at 0°.

Ex. 12.—Analysis of a sample of commercial oxygen, using the ammoniacal-cuprous-oxide pipette.

The ammoniacal-cuprous-oxide pipette is a Hempel pipette for solids and liquids, having the cylindrical portion filled with little rolls of copper gauze immersed in a solution of ammonium carbonate in aqueous ammonia.

• To carry out the analysis 100 cu cm. of oxygen are first measured in a burette. The oxygen is obtained direct from a cylinder fitted with a reducing valve. To obtain a fair sample the gas should be allowed to escape for a few seconds before passing the portion taken for analysis into the burette.

The burette is now connected with the pipette in the usual manner, and the gas transferred to the latter. The

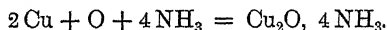
pipette may be allowed to remain quietly until the absorption is complete, as a sufficient amount of reagent will remain entangled in the meshes of the gauze to absorb the whole of the oxygen. It is better, however, particularly when working with gases containing a high percentage of oxygen, as in the present case, to transfer the gas several times from burette to pipette and back again, so that the upper part of the gauze is constantly wetted with fresh reagent. Very rapid absorption is thus brought about. When the absorption is complete the residual gas is returned to the burette and measured.

The result obtained will vary between 88 per cent and 99 per cent by volume of pure oxygen.

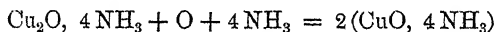
The little rolls of copper gauze, before introducing into the pipette, require to be treated with dilute nitric acid, as they are usually covered with a thin layer of fatty matter which hinders the absorption. The liquid in which they are immersed is prepared by mixing equal volumes of a saturated solution of ammonium carbonate and a solution of ammonia of sp gr 0.96.

The reaction between copper, ammonia, and oxygen probably takes place in stages according to the following scheme —

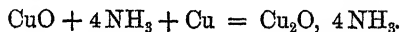
A colourless compound of cuprous oxide and ammonia is first formed according to the equation



This compound is then able to take up a further atom of oxygen to form the corresponding deep-blue cupric compound



The excess of copper always present then reacts with this cupric compound, re-forming the cuprous compound



According to these equations 1 g of copper is able to absorb 177 cu cm of oxygen, the absorption value being thus very high. An ammoniacal cuprous oxide solution, like an alkaline solution of sodium hyposulphite, has the great advantage over alkaline pyrogallol and phosphorus of being able to absorb oxygen without being affected by temperature, so that it is immaterial whether the absorption be carried out at 0° or 20°.

The copper pipette has, however, the serious drawback that it is able to absorb carbon monoxide, and consequently gas mixtures which contain this gas cannot be analysed with it. In this respect an alkaline hyposulphite pipette is to be preferred, as this does not absorb carbon monoxide.

Copper can also be used as an absorption reagent for oxygen in another manner, viz in the form of the red-hot metal. This method is particularly useful in the exact determination of the amount of oxygen in atmospheric air. The method was first proposed by *Jolly*, but has been considerably improved by *Kreusler*. The analysis is carried out by heating a copper wire to redness electrically in a measured volume of air at known temperature and pressure. The oxygen then combines with the copper to form copper oxide. After absorption is complete, and the gas has cooled down, the reduction in pressure is measured, and from this the amount of oxygen present can be calculated.

Another reagent which is often used to absorb oxygen is a solution of chromous chloride in hydrochloric acid. This is the only reagent which can be used for this purpose in the case of gas mixtures containing sulphuretted hydrogen, or to determine the amount of oxygen in sulphuretted hydrogen gas.

The reagents used for absorbing oxygen which have been already mentioned, viz alkaline pyrogallol, phos-

phorus, ammonio-cuprous oxide, sodium hyposulphite, and chromous chloride, are the most important

Their relative advantages and disadvantages may be again briefly repeated —

Alkaline pyrogallol.—The absorption value is low, and the rate of absorption is greatly dependent on the temperature. It can, however, be used in nearly all cases

Phosphorus—Working with this substance is not entirely free from danger, the rate of absorption, as in the case of alkaline pyrogallol, is greatly dependent on the temperature, the power of absorption fails when certain substances, like ethylene, sulphuretted hydrogen, oil of turpentine, &c, are present in the gas mixture to be analysed. On the other hand, the absorption value is very high, and absorption proceeds rapidly at ordinary temperatures

Ammonio-cuprous oxide—Cannot be used for gases containing carbon monoxide. It has, like the phosphorus pipette, a high absorption value, but this is independent of temperature

Sodium hyposulphite—The slightly alkaline solution of this substance is pleasanter and cleaner to work with than the strongly alkaline, deep-brown solution of pyrogallol, and is moreover considerably cheaper. The absorption value is high, and is independent of temperature. It is unaffected by the substances which cause the phosphorus pipette to fail, and unlike ammonio-cuprous oxide it does not absorb carbon monoxide. An alkaline solution of sodium hyposulphite is therefore the most suitable reagent for the absorption of oxygen in most cases.

Chromous chloride.—This is rather tedious to prepare, but is the only reagent which can be used in the case of gas mixtures containing sulphuretted hydrogen,

Ex. 13.—Analysis of a mixture of carbon dioxide, oxygen, carbon monoxide, and nitrogen (flue gas), using the Hempel apparatus.

Exactly 100 cu. cm of flue gas are first measured in a Hempel burette over carbon dioxide water. The carbon dioxide present is first absorbed with the potash pipette, and then the oxygen with the pyrogallol or hyposulphite pipette.¹ For the absorption of carbon monoxide a pipette containing an ammoniacal solution of cuprous chloride is employed. The gas is first shaken for 3 min. in a cuprous chloride pipette marked I, and then for a further 5 min in a second similar pipette marked II (The reason for this procedure is fully explained below) The residual gas is then transferred back to the burette and measured

Example—

Volume of gas measured	100 cu. cm
After absorption with KOH	.	.	.	86.2 "
∴ CO ₂ = 100 — 86.2	13.8 "
After absorption with hyposulphite				73.6 "
∴ O = 86.2 — 73.6				12.6 "
After absorption with cuprous chloride	.	.	.	57.8 "
∴ CO = 73.6 — 57.8	15.8 "

The gas mixture therefore contains

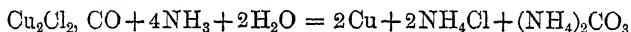
13.8	per cent	CO ₂
12.6	"	O
15.8	"	CO
57.8	"	N

The ammoniacal solution of cuprous chloride used for filling the pipette is prepared by dissolving 7 g of cuprous chloride in 100 cu cm. ammonia of specific gravity 97. Such a solution has a dependable absorption value of about 6 cu cm carbon monoxide.

¹ Before returning the gas from the potash pipette to the burette the water in the latter must be changed (see Ex. 9)

In the absorption of carbon monoxide by a solution of cuprous chloride, there is formed copper-carbonyl chloride, $\text{Cu}_2\text{Cl}_2 \cdot \text{CO}$. Either a hydrochloric acid or an ammoniacal solution of cuprous chloride can be used. In working with the Bunte burette (to be described later), a hydrochloric acid solution is usually employed, but for filling the Hempel pipette an ammoniacal solution is to be preferred on the following grounds:—

If an ammoniacal solution of cuprous chloride containing carbon monoxide is allowed to stand for some time, metallic copper slowly separates, the carbon monoxide disappears, and ammonium carbonate is formed



The solution becomes, therefore, poorer in carbon monoxide, and the precipitated copper also protects the cuprous chloride from oxidation as well as reducing any cupric compound present to the cuprous state. This reaction does not take place in presence of hydrochloric acid, any carbon monoxide absorbed remaining in solution. An ammoniacal cuprous chloride solution has therefore a much higher absorption value than an acid solution.

In absorbing carbon monoxide by means of cuprous chloride it is necessary to remember that the combination between these two substances is a very loose one. By boiling the solution, placing it in a vacuum, or by shaking with an indifferent gas, the carbon monoxide can be entirely or partially liberated. If a cuprous chloride pipette has been repeatedly used for absorbing carbon monoxide, it can happen that the gas is no longer completely absorbed. If the gas to be investigated is very poor in carbon monoxide it may even happen that instead of the volume diminishing it actually increases, the highly charged cuprous chloride solution having liberated carbon monoxide. This is more particularly

likely to occur when a hydrochloric acid solution is used, but it can also happen when using an ammoniacal solution, as the previously mentioned disappearance of carbon monoxide requires some time. In order, then, to avoid this danger two cuprous chloride pipettes are usually used. The gas is first shaken with a pipette which has been some time in use, when the greater proportion of the carbon monoxide is removed. It is then shaken in a second pipette which has been little used, when the residue is absorbed. Only by working in this way can concordant results be obtained.

It is also necessary to note that carbon monoxide is not absorbed by cuprous chloride solution with anything like the rapidity with which oxygen is absorbed by pyrogallol or phosphorus, or carbon dioxide by caustic potash, but that continual vigorous shaking of several minutes' duration is necessary to obtain complete absorption.

It is also necessary to observe that acetylene, ethylene, and oxygen are taken up by cuprous chloride solutions, and these gases must therefore be previously removed before the estimation of carbon monoxide.

When it is at all possible it is best in carrying out gas analyses always to take 100 cu cm of the gas in question, as then the result is obtained direct in volume percentages without any further calculation. The residual gas, after removing the total absorbable and combustible gas constituents, is regarded as nitrogen, and as such set down in the result. It is very difficult to carry out a direct determination of nitrogen.

Ex. 14.—Analysis of a mixture of carbon dioxide, oxygen, carbon monoxide, nitrogen, and ethylene with the Hempel apparatus.

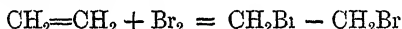
100 cu cm of the mixture are first measured over carbon dioxide water. The carbon dioxide is first

absorbed (*liquid in burette then changed*), and then the ethylene absorbed by means of a biomine pipette. The gas is shaken in this 5 min. On returning the gas to the burette a considerable amount of bromine vapour is carried over, and as this exerts a considerable tension it is necessary to remove it before reading off the volume of the gas. This is done by passing the gas into a potash pipette, and then back to the burette. The oxygen is then determined by means of pyrogallol or sodium hyposulphite, and then the carbon monoxide by the use of two cuprous chloride pipettes. The residue is nitrogen.

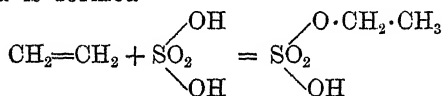
The result is set out exactly as in the previous exercise.

The bromine pipette is filled with a saturated aqueous solution of bromine. A few drops of biomine should be put into the pipette, so that the solution may always remain saturated.

Bromine reacts with ethylene in such a way that two atoms of bromine add on to the double bond to form a liquid ethylene bromide



Fuming sulphuric acid may also be used in place of bromine to absorb ethylene, and in this case ethyl sulphuric acid is formed.



Fuming sulphuric acid is, however, a highly corrosive substance, and in working with this reagent it is of the greatest importance to protect the connecting tubing from coming in contact with the reagent. Strict precautions must also be taken to prevent any water entering the pipette, as this might easily lead to an explosion. For these reasons fuming sulphuric acid is a very tedious

substance to work with, and the use of bromine water is to be preferred

Besides absorbing ethylene, bromine water can also absorb its homologues, propylene, C_3H_6 , and butylene, C_4H_8 , also acetylene, C_2H_2 , and the aromatic hydrocarbons, benzene, C_6H_6 , and toluene, C_7H_8 , the vapours of which occur in many gas mixtures, e.g. illuminating gas. Ethylene, propylene, butylene, and acetylene are converted into bromine compounds, whilst the aromatic hydrocarbons, benzene and toluene, are mechanically absorbed. The above-mentioned gases and vapours are usually described as "heavy hydrocarbons", as distinct from the "light hydrocarbons", methane and ethane.

The decrease in volume obtained on treating a gas mixture with bromine water is not put down in the result as ethylene, but as heavy hydrocarbons, except where it has previously been proved that only one particular member of the class is present in the mixture.

The presence of heavy hydrocarbons is always to be expected when the gas under investigation has been obtained by the distillation of organic bodies, e.g. in coal gas, oil gas, &c.

Ex. 15.—Determination of the amount of oxygen in the air by means of the *Franke* burette.

The *Franke* burette (fig. 10) consists of a reagent compartment B and a measuring compartment A. These can be separated by the wide bore tap b.

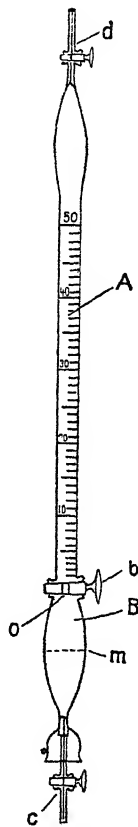


Fig 10

The measuring tube ends in a capillary tube, with an ordinary glass tap *d*. The reagent tube can be closed by a well-ground glass cap *c*, which has also a glass tap. The measuring tube holds 100 cu cm, and has the zero point at the bottom of the bore of the tap at 0.

In order to measure 100 cu cm of air or any other gas, the cap *c* is removed, and the whole apparatus completely filled with water. The cap is then replaced, and the complete apparatus hung in a retort stand in the position shown in the diagram. The capillary *d* is then attached to the gas source, all taps opened, and gas allowed to enter until the water level has fallen to about the position *m*. The tap *d* is then closed, and the apparatus placed in a tall vessel of water and adjusted until the level of the water inside and out is the same, and tap *b* closed in this position. There are then 100 cu cm. of gas enclosed in the measuring tube at the prevailing temperature and pressure. If considerable quantities of gas are available, the burette may also be filled by allowing the gas to stream for some time through the burette, and then first closing the tap *d* and then the tap *b*. There are then 100 cu cm. of gas enclosed in the measuring vessel. To carry out the exercise 100 cu cm of air are first measured, and then the water is emptied completely from the reagent compartment. The burette is then fastened in the tripod stand in an inverted position to that shown in the diagram. The reagent vessel is now filled with a reagent for absorbing oxygen (alkaline pyrogallol or sodium hyposulphite solution), and the cap *c* replaced with the tap open in such a way that no air bubbles are enclosed, and the capillary is completely filled with the reagent. The tap is then closed. It is necessary to be quite sure that no air bubbles remain in the reagent vessel. The tap *b* is then opened. The reagent trickles slowly out

of the reagent compartment into the measuring compartment, and spreads itself over the walls of the tube. At the same time the gas bubbles through the reagent, and gradually fills the reagent vessel. In this way the gas comes into intimate contact with the reagent. When the whole of the latter has run into the measuring tube the burette is inverted, and the liquid allowed to flow back to the reagent vessel. This operation can be repeated until it is quite certain that all oxygen is absorbed. The absorption liquid is then allowed to collect completely in the reagent vessel.

(Wait five minutes, using sandglass.)

When this is again completely full, the tap *b* is closed, the glass cap removed, and the reagent returned to the stock bottle. The reagent vessel is then rinsed out with clean water, filled with distilled water at room temperature, and the glass cap *c* replaced. The tap of *c* is now opened, and the whole burette with *c* underneath immersed in a tall cylinder of water, and *b* opened. As much water then rises into the burette as oxygen has disappeared. When the water level inside and outside the burette is the same, the volume of residual gas is read off.

It occasionally happens that the absorption liquid, after flowing back into the reagent compartment, does not fill this completely. If the tap *b* were now closed, it would not be possible to empty out the reagent without also losing the enclosed gas bubble, and thus obtaining too high a result. This may be remedied by pouring a little of the reagent into a shallow porcelain dish, dipping into this the capillary of the cap *c*, and opening the tap until sufficient liquid has been drawn in to fill the reagent compartment.

To analyse a complicated gas mixture by the aid of the *Franke* burette, the method of procedure is exactly as described above. If the analysis of a flue gas, for

example, is to be made, carbon dioxide is first absorbed with caustic potash, and the resulting diminution in volume measured. The reagent vessel is then filled with an alkaline solution of sodium hyposulphite, the oxygen present absorbed with this, and the diminution in volume again measured.

To estimate carbon monoxide, using a solution of cuprous chloride, the water contained in the measuring compartment must first be removed, so that the reagent may not be too much diluted. This is carried out by means of a pressure and suction bottle in exactly the same way as in the *Bunte* burette, under which the method of procedure is described. When this has been done, the absorption of carbon monoxide is carried out with an ammoniacal solution of cuprous chloride.

The inventor of the *Franke* burette claimed for it many advantages, particularly over the *Bunte* burette. Its simple construction, and the possibility of recovering the various reagents to be used over again, were emphasized, as well as the fact that it was not necessary to connect with a suction apparatus as often as with the *Bunte* burette. Its construction is, however, not simpler than that of the *Bunte* burette, and also only the first-used reagent can be recovered undiluted, the second reagent being diluted by the water remaining in the measuring vessel after taking the first reading. With reference to the use of a suction bottle, this is always necessary in the analysis of complex gas mixtures, as illustrated by the analysis of flue gas described.

Ex. 16.—Determination of the amount of oxygen in air by means of the *Bunte* burette.

The *Bunte* burette (fig. 11) consists of a measuring tube, which is closed at the top by a three-way tap *a*,¹

¹The *Winkler* and *Greiner-Friedrich* three-way taps are the types usually

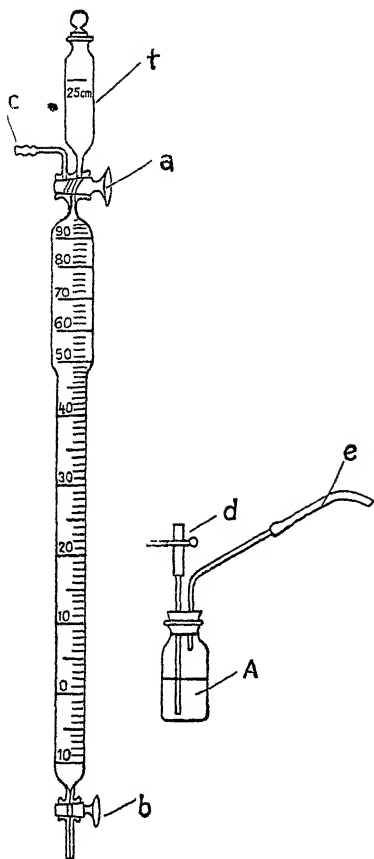


Fig. 11

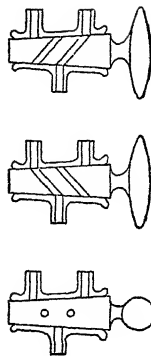


Fig. 12

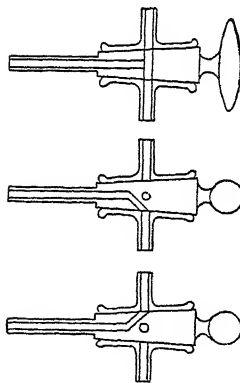


Fig. 13

and below by an ordinary glass tap *b*. Connected with the three-way tap is a vessel *t*, provided with a mark, used. The Winkler tap, with the connections which are possible with it, is best understood from fig. 13.

The *Greiner-Friedrich* tap, with its connections, is shown in fig. 12. Instead of having a bore at right angles and one through the length of the tap, as the Winkler tap has, this has two holes bored obliquely through the key of the tap.

and a short piece of capillary tube 4-5 cm. long is fused to *b*. The measuring tube holds rather more than 100 cu cm, the 100 mark being placed at the lower end of the capillary of the three-way tap and the zero at the lower end of the tube, the calibration being continued for a further 10 cu cm below the zero mark. Each cubic centimetre is further subdivided into $\frac{1}{5}$ cu cm.

In order to measure 100 cu cm of air or other gas in the Bunte burette, a long rubber tube attached to a funnel is first connected with the lower capillary, the tap *b* opened, and the three-way tap so arranged that the inside of the tube communicates with the outside air. Water is then poured into the funnel until the measuring tube and the capillary of the three-way tap is completely full. The tap is then turned so as to put the measuring tube in connection with the small vessel, and this also filled with water up to the mark. The taps are then closed, and the rubber tube and funnel removed. The side tube *c* is then connected with the source of gas, the tap *a* placed in communication with the inside of the tube, and the lower tap *b* then opened. Water flows out, and the gas enters to take its place.

About 2 or 3 cu cm more than the required 100 cu. cm are allowed to enter, and then both taps are closed. A few minutes must be allowed for the water which adheres to the walls of the tube to coalesce and run down.

In order now to measure exactly 100 cu. cm of gas, a pressure and suction flask *A* is necessary. The construction of this is readily seen from the diagram. The piece of rubber tubing *d* of the pressure flask is provided with a pinchcock, and the flask contains a small amount of water.

By blowing through the rubber tube *e* and opening the pinchcock, *d* is completely filled with water, and is

then connected to the capillary tube below the tap *b*. This is then opened, and by blowing into *e* and keeping the pinchcock open, the gas is compressed until the level of the water is above the mark 0. The pinchcock is then closed. By carefully squeezing the pinchcock, water is allowed to run out from the measuring tube again until the meniscus stands at about 2 cu cm below the zero mark. There are now enclosed in the burette 100.2 cu cm of gas at the room temperature, but at a pressure greater than atmospheric pressure. In order to bring the gas under a pressure which is comparable, the three-way tap is turned to bring the interior of the measuring tube into communication with the small attached vessel *t*. The excess gas then escapes through the water contained in this, and about 2 cu cm. water finds its way into the measuring tube, the capillary filling again with water. The water which has entered gradually runs down the walls, and the under meniscus then stands exactly at 0. There are now enclosed in the measuring tube 100 cu cm of gas at the prevailing temperature, and at a pressure equal to that of the atmosphere plus the pressure of the column of water in the small vessel. In measuring the residual gas after absorption of the various constituents the pressure must remain the same as this.

In order to introduce the absorption reagent into the burette the tap *b* is opened, and after opening the pinchcock, suction is applied to the rubber tube *e*, until the greater portion of the water is removed from the burette, the level falling to just above the tap *b*, which is then closed, and the suction bottle removed. The absorption reagent—in the case of oxygen, alkaline sodium hyposulphite solution—is then poured into a small porcelain dish, the lower capillary of the burette dipped into it, the tap opened, and the reagent allowed to ascend into

the tube The tap *b* is then closed, and the burette taken out of the retort stand after closing the glass vessel with its well-ground glass stopper The burette is then held by the three-way tap and the ordinary tap *b*, as far as possible without handling the measuring tube, and the reagent brought into intimate contact with the gas by inclining the tube in various directions After shaking several times, the lower capillary is again dipped into the reagent, the tap opened, and fresh liquid allowed to enter After thoroughly shaking for 3 min, the burette is again returned to the stand, the glass stopper removed, and the pressure and suction bottle again attached after filling the tube *d* completely with water The tap *b* is then opened, and by sucking through the tube *e* a vacuum is produced in the bottle By opening the pinchcock carefully the reagent is transferred from the tube to the bottle, which should be done as completely as possible.

The three-way tap is then turned so that the small vessel communicates with the measuring tube, and 2 to 3 cu cm water are allowed to flow slowly down the walls of the tube, taking with it the drops of reagent adhering to the tube The rinse-water is removed by the suction flask, and the rinsing repeated. The glass vessel is then filled to the mark with distilled water, the suction flask removed, the under capillary dipped into a porcelain basin containing distilled water, and by opening the tap *b* the water is allowed to enter. The tap *b* is then closed, and the three-way tap turned to put the measuring tube in communication with the glass vessel Water flows into the burette, and the gas then is under the same conditions of pressure as it was originally measured under, viz the atmospheric pressure plus the pressure of the water column in the glass vessel After closing the three-way tap a short time is allowed

for the water to collect, and the volume of gas then read off

Result.—20.4 to 20.6 per cent O

The Bunte burette is certainly the most suitable apparatus to carry out rapid gas analyses. The only requirements are the burette itself, a rubber tube and funnel, a pressure bottle, a porcelain dish, and bottles of the various reagents. In working with the Hempel apparatus there are required a burette and a large number of absorption pipettes. If the Bunte burette is correctly manipulated, the results are just as good as with the Hempel apparatus.

In removing the absorption reagent from the burette, it is not allowable, as is however often done, to open the tap *b*, and to open the three-way tap so that water flows in a continual stream from the glass vessel through the burette carrying the reagent with it. In this way a considerable error may be introduced. On the one hand, the more readily soluble constituents may be removed from the gas mixture, and on the other, gases dissolved in the wash water may diffuse out into the gas to be analysed.

Ex. 17.—Analysis of flue gas with the Bunte burette.

100 cu. cm of the gas are first measured in a Bunte burette in the manner described in the previous exercise, but using carbon dioxide water as the confining liquid. The carbon dioxide is first absorbed with caustic potash solution, and the diminution in volume measured over *distilled* water. The oxygen is then absorbed with alkaline hyposulphite, and finally carbon monoxide is absorbed either with an ammoniacal or a hydrochloric acid solution of cuprous chloride. In carrying out the absorption

of carbon monoxide with cuprous chloride, 10 cu. cm. of reagent are first introduced, and after shaking well, removed, and a second fresh supply introduced. This is repeated a third time. If the absorption of carbon monoxide has been carried out with a hydrochloric acid solution of cuprous chloride, the walls of the tube must not be washed down with distilled water, as this would precipitate solid cuprous chloride. In this case 3-4 cu. cm. of concentrated hydrochloric acid are poured into the glass vessel, and allowed to trickle down the walls of the tube. This is then followed with a few cubic centimetres of distilled water, and finally washed again with distilled water.

The result is set out exactly as shown in Ex. 13.

The cuprous chloride solution used for the absorption of carbon monoxide is prepared by placing 10 g. of cuprous chloride in a bottle holding 250 cu. cm., putting in a copper spiral reaching from the bottom to the neck of the bottle, and filling up with concentrated hydrochloric acid. After shaking well, the whole is set aside in a dark place until the colour has entirely disappeared.

In sucking out the reagents from the Bunte burette there are sometimes difficulties experienced, as after the last absorption there is a strong back suction in the burette. The suction should never be done with the lungs, but always with the mouth. If difficulties are experienced, the rubber tubing *c* of the suction bottle may be fitted with a pinchcock, and then attached to a water pump. The bottle can thus be exhausted, and the absorption liquid readily transferred from the burette.

Ex. 18.—Analysis of a mixture of flue gas and ethylene with the Bunte burette.

The gas mixture is first measured over water satu-

rated with carbon dioxide. The individual constituents are then absorbed in the following order, exactly as in Exercise 14 —

- 1 Carbon dioxide.
- 2 Ethylene
- 3 Oxygen
- 4 Carbon monoxide.

Saturated bromine water is used as the absorption reagent for ethylene, about 10 cu cm being allowed to ascend into the burette and vigorously shaken with the gas.

If the gas does not remain coloured with the bromine vapour, or should the bromine water be completely decolorized, the exhausted reagent must be removed, a fresh supply introduced, and the shaking repeated. The excess of bromine water is then removed by suction, first taking the precaution to add a small amount of caustic potash solution to the water in the suction flask. To remove the bromine vapour from the burette a little caustic potash is introduced, and the burette then rinsed out with water. In all other respects the exercise is carried out exactly as described in Ex. 16 and 17.

Ex. 19.—Analysis of furnace gases by means of the *Orsat* apparatus.

The *Orsat* apparatus (fig. 14) consists of a measuring tube A, surrounded by a water jacket to prevent change of temperature, and three absorption vessels B, C, D. The measuring tube has a capacity of 100 cu cm., and is wider at the top than at the bottom. The bottom of the measuring tube ends in a side tube, to which is attached a long piece of rubber tubing fitted with a pinchcock *b* and a levelling bottle E. The top of the measuring tube ends in a capillary tube in connection

with the absorption vessels. Each absorption vessel consists of two glass cylindrical bulbs of equal capacity connected at their lower extremities by a bent glass tube, one cylinder ending in a capillary with a mark on the glass, and the other with a tubulure. The absorption vessels are filled with the various absorbing reagents,

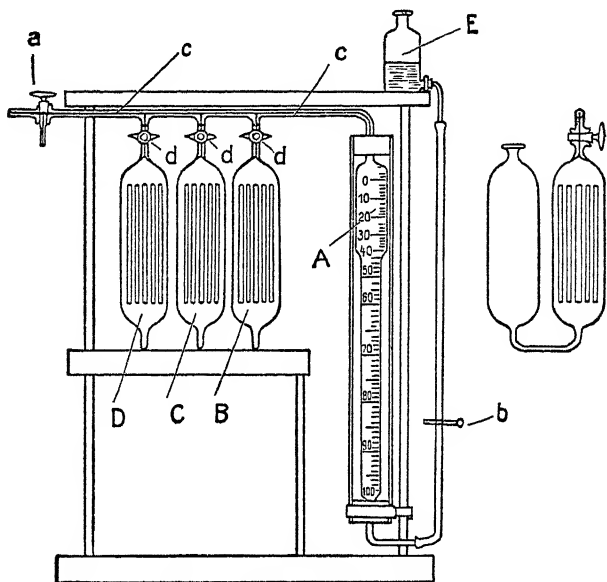


Fig 14 — Orsat Apparatus

the cylinder with the capillary tube also containing lengths of glass tubing to increase the surface area.

The measuring tube is connected with the absorption vessels by the capillary tube *cc*, which carries several branches with ordinary glass taps *d*. Both the measuring tube and the absorption vessels are connected to this capillary tube by means of short pieces of stout rubber tubing. The free end of the capillary tube is closed

by a three-way tap *a*. The whole apparatus is mounted securely on an iron or wooden stand so as to be readily portable.

To prepare the apparatus for use, the absorption vessel *B* is filled with caustic potash solution, *c* with alkaline pyrogallol, *D* with ammoniacal cuprous chloride, and the levelling bottle with water.

The taps *d* are then closed, the three-way tap turned so that the capillary tube is in communication with the outside air, and the measuring tube then filled with water to the mark 0 by raising the levelling bottle and opening the pinchcock. The tap *a* is then closed. The whole of the air is next removed from the caustic potash vessel by opening the tap *d*, squeezing the pinchcock *b* until the caustic potash solution has risen to the mark on the capillary tube, and again closing *d*. Care must be taken not to allow the solution (as also the other absorption reagents) to rise above the mark, as should it come in contact with the tap, this becomes very soon cemented in its seat by the solid crystallizing out. The other absorption vessels are filled to the mark in exactly the same manner, and the measuring tube again filled up to mark 0 with water. The apparatus must now be tested to make sure that all joints are gas-tight. To do this the pinchcock *b* is removed, and the whole apparatus allowed to stand for some time. If the level of the liquid in the measuring tube and in the absorption vessels does not sink, then the apparatus may be regarded as satisfactory.

The gases to be examined with this apparatus are obtained from a furnace or other source of combustion. In the first case the gases in contact with the glowing fuel are to be analysed, and then the final gaseous combustion products.

To sample the gas in contact with the incandescent

fuel an iron tube is sunk in the midst of it, and to the projecting end of this is attached a glass tube, filled with asbestos or glass wool, by means of rubber tubing. This serves to retain particles of soot or ash which may be mechanically carried over. The other end of the glass tube is then connected to one free end of the three-way tap *a* of the apparatus. To the other end of the tap *a* is attached a rubber hand pump,¹ and the tap so turned that the tube of the rubber pump is in connection with the tube leading to the source of the gas. By means of the pump, the whole of the connecting tubes can be filled with the gas to be tested (about ten squeezes are sufficient), and when the tubes are quite full they are placed in communication with the measuring tube by means of the three-way tap. The pinchcock *b* is then opened, and rather more than 100 cu. cm. gas allowed to stream into the measuring tube. The tap *a* is then closed, and the tube connections as well as the hand pump removed. In order now to enclose exactly 100 cu. cm. of gas in the measuring tube, the tap *a* is connected with the outside air, the surface of the water in the levelling bottle adjusted to the level of the 100 cu. cm. mark, and the pinchcock squeezed. The excess gas thus escapes, and the level of the water in the tube rises to the 100 mark, giving when *a* is again closed exactly 100 cu. cm. gas at the prevailing temperature and pressure.

¹ The rubber pump (fig. 15) is a long rubber ball or bulb, to both ends of which are attached lengths of rubber tubing. Two valves opening in opposite directions are fitted inside the bulb. When the bulb is compressed in the hand, one valve opens and the air is forced out. When the pressure is released, this valve closes and the second valve opens, air being drawn through this until the bulb regains

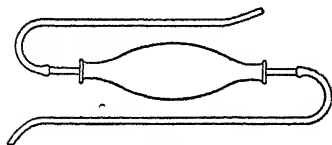


Fig 15

its normal size. In attaching the pump to the Orsat apparatus, the inlet or suction tube is attached to the tap *a*, whilst the exit tube remains free.

To absorb the carbon dioxide the tap on the potash vessel B is opened, and the gas transferred over by raising the levelling bottle and opening the pinchcock. The water is allowed to enter the measuring tube until it reaches the mark 0

To return the gas the levelling bottle is lowered, and the pinchcock kept open until the caustic potash has risen to its original level mark. In carrying out these operations, care must be taken not to allow either water or caustic potash solution to enter the capillary tube. The tap *d* is then closed, and the levelling bottle raised until the level of the water in it is the same as the level inside the tube, the pinchcock being open. When the level is adjusted the pinchcock is closed, and as the gas now stands under atmospheric pressure the volume of carbon dioxide which has been absorbed can be read off.

The whole operation is then repeated, and the volume again read off. If the reading does not agree with the first reading, the operation must be repeated once more. The absorption of oxygen in the pyrogallol vessel and carbon monoxide in the ammoniacal cuprous chloride vessel is carried out in an exactly similar manner. In order to accelerate the rate of absorption in these latter cases, it is advisable to transfer the gas repeatedly backwards and forwards from the absorption vessel to the measuring tube, so that the surface of the glass tubes may be continually wet with fresh reagent.

To obtain a sample of the final gaseous products of combustion, the iron tube should be inserted as far as possible into the flue or chimney through which these are being led away, the gas being transferred to the apparatus exactly as described above.

The results of the analysis should then be set out as shown in Exercise 13.

After some practice, it is possible to carry out an

analysis with the Orsat apparatus in about 5 min. The results are not so exact as those obtained with the Hempel apparatus or the Bunte burette, but are sufficiently accurate for technical purposes, e.g. the control of furnace combustion. Besides the particular form of Orsat apparatus described, there are many other forms in use, which, however, all work on the same principle. Many have fitted to them an arrangement permitting of combustion analyses, whilst in others the vessel for cuprous chloride is missing, so that only carbon dioxide and oxygen can be estimated.

Ex. 20.—Estimation of hydrogen by burning with oxygen in the explosion pipette.

The *explosion pipette* (fig 16) consists of two thick-walled glass bulbs, A and B, which are connected by a

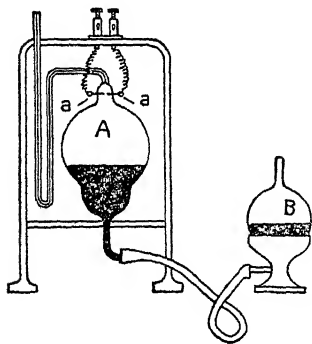


Fig 16

protected or armoured rubber tube. A is mounted on an iron stand, and ends at the top in a simple bent capillary tube, at the end of which is a piece of rubber tubing. B is supported in a heavy iron foot. Two platinum wires are fused into the upper part of the bulb A, the ends being 1 to 2 mm apart inside. Between the ends of these wires an electric spark can be passed to

explode a mixture of oxygen and hydrogen. The wires end outside the bulb in two loops, to which can be attached the wires from an induction coil. Sufficient mercury is placed in the bulbs to allow of the explosion bulb A being completely filled when B is raised.

To carry out the experiment about 20 to 25 cu. cm.

of hydrogen, obtained either from a Kipps apparatus or an electrolytic hydrogen generator, are measured in a Hempel burette. This is then mixed with air by placing the levelling tube, after emptying out most of the water, on the floor, the measuring tube being on the table, and cautiously opening the pinchcock. Sufficient air is allowed to enter to give a total volume of about 100 cu cm. The exact volume is then measured. A connecting capillary tube is then attached to the rubber tube of the explosion bulb A, and the latter closed by a pinchcock. By raising the bulb B, and cautiously opening the pinchcock, the explosion bulb with the rubber connection and connecting capillary are completely filled with mercury, and the latter is then pushed into the rubber connection of the Hempel burette, this having previously been filled with water. By lowering B, opening the pinchcocks, and raising the levelling tube of the burette, the gas is transferred to the explosion bulb. The levelling tube must be kept raised until a drop of water enters the bulb. The platinum wires are then connected with an induction coil, and after lowering the bulb B to put the explosive mixture under a considerably reduced pressure, the circuit is closed, and a spark passed between the platinum points inside the bulb, when an explosion takes place. The levelling bulb is then raised, and the residual gas transferred to the burette, care being taken that no mercury is carried over into the measuring tube. After waiting 5 min., the contraction in volume is measured. The volume of hydrogen present is equal to $\frac{2}{3}$ of the contraction.

The amount of oxygen present in the residual gas should then be determined, and from the amount of oxygen which has disappeared the hydrogen again calculated. In this case the hydrogen is equal to twice the volume of oxygen used up.

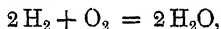
Example.—

Hydrogen measured	21 6 cu cm
Total volume	98 4 „
∴ Air (98 4 — 21 6)	76 8 „
Containing oxygen	16 1 „
Oxygen theoretically necessary for combustion	10 8 „
∴ Excess of oxygen present	5 3 „
Volume of gas after explosion	66 3 „
Contraction, 98 4 — 66 3	32 1 „
∴ Hydrogen, $\frac{32\ 1 \times 2}{3}$	21 4 „

Calculation of volume of hydrogen from the volume of oxygen used up

Residual gas after explosion	66 3 cu cm
After absorption with pyrogallol	60 9 „
Oxygen present, 66 3 — 60 9	5 4 „
Oxygen used up, 16 1 — 5 4	10 7 „
∴ Hydrogen, $10\ 7 \times 2$	21 4 „

The combination of hydrogen and oxygen takes place according to the equation



2 volumes hydrogen and 1 volume oxygen giving 2 volumes water vapour. As, however, the experiment is carried out at ordinary temperatures, the water vapour condenses to liquid water, and the contraction is equal to 3 volumes. Two volumes of hydrogen on explosion therefore give a contraction of 3 volumes, and inversely the amount of hydrogen present is obtained by multiplying the contraction by $\frac{2}{3}$.

Ex. 21.—Estimation of hydrogen by burning with oxygen with the aid of the palladium-asbestos capillary.

If a mixture of oxygen and hydrogen be passed over gently warmed metals of the platinum group, and more

especially palladium, combination takes place at a temperature very considerably lower than that required to bring about combination by explosion. *Winkler* found that the union of the two gases took place very readily when the mixture was passed over asbestos covered with finely divided palladium.

The palladium-asbestos capillary consists of an ordinary connecting capillary tube, into which has been loosely inserted a little roll of asbestos impregnated with palladium (fig 17). In order to carry out an analysis with this tube, it is first inserted in the rubber end-tube of a water pipette, provided with a pinchcock. The water must not be allowed

to enter the capillary, as otherwise, on subsequent heating, the glass would be liable to crack. The height of the water in the water



Fig 17

pipette must therefore be marked with an oil pencil or strip of gummed paper. A mixture of air and hydrogen is then prepared as described in the previous exercise, the rubber end-tube of the Hempel burette attached to the palladium capillary, and the pinchcock removed from the pipette tubing. The palladium capillary is then heated gently for one or two minutes, but not sufficient to soften the glass or to heat the tube to redness, the levelling tube stood on the table, and by opening the pinchcock the gas transferred slowly over the heated asbestos into the water pipette, the heating being continued. It will be noticed that the end of the asbestos plug nearer the burette glows brightly. The gas must be transferred so as to leave only $\frac{1}{2}$ cu cm in the burette. It is then, after putting the levelling tube at a low level, slowly transferred back to the burette until the water in the pipette reaches its marked position.

The whole operation must be repeated, and then the resulting diminution in volume read off. In order to be quite sure that all the hydrogen is burnt, the gas should be led backwards and forwards once again over the heated palladinized asbestos, and the volume again read off. The volume should remain the same.

The result should be calculated exactly as described in Ex. 20.

Ex. 22.—Fractional combustion of hydrogen and methane by means of the palladium-asbestos capillary and the Winkler combustion pipette.

If a mixture of hydrogen, methane, and air is passed over gently heated palladinized asbestos, the hydrogen burns whilst the methane remains unaltered. The homologues of methane—e.g. ethane—behave in exactly the same way. Advantage can therefore be taken of this peculiar behaviour to estimate hydrogen in presence of methane and its homologues.

This method is of particular importance when it is required to analyse a gas mixture consisting of hydrogen and two homologues of methane. A mixture of hydrogen and one methane homologue can be analysed by first mixing with air, exploding the mixture, and determining the contraction and the amount of carbon dioxide produced. This method of procedure is, however, not possible in the case of a mixture of hydrogen and two homologues of methane. According to *Haber*, "it is not possible to calculate the composition of a mixture of methane homologues and hydrogen if only the contraction, amount of oxygen used up, and amount of carbon dioxide formed is known,* for there will either be no or an unlimited number of mixtures of hydrocarbons and hydrogen which will satisfy the three figures obtained. It is therefore necessary to obtain one of the required figures

independently" This can be done by a fractional combustion of the hydrogen alone, using palladinized asbestos or a gently heated palladium wire To carry out the analysis 100 cu cm of the gas mixture are first measured, and any CO_2 , O, or CO which may be present absorbed by suitable reagents 10-15 cu cm of the non-absorbable residue are measured and mixed with air to nearly 100 cu cm The mixture is then led over heated palladinized asbestos exactly as described in the previous exercise The contraction thus produced is measured, and from this the amount of hydrogen present is calculated In order to prove that no methane has been burnt, the gas should be passed into a potash pipette, when there should be no diminution in volume on returning it to the burette The combustion of the methane is then brought about in a *Winkler* combustion pipette (fig 18) This consists of a large Hempel pipette for solids and liquid, in the tubulure of which is inserted a two-holed rubber stopper, through which pass two brass electrodes The electrodes are connected inside the pipette by a piece of thin platinum wire, and are attached to binding screws outside the pipette Before commencing the analysis the electrodes are connected with a suitable source of electricity.

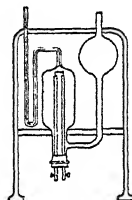


Fig 18

The burette is then connected with the pipette in the usual manner, the levelling tube raised high with the left hand, and the pinchcock gradually opened with the right The gas then passes over into the pipette, and immediately the water above the electrodes is displaced the platinum wire glows brightly, and combustion commences The stream of gas should be stopped for a moment by closing the pinchcock until the first vigorous reaction is over. The remainder of the gas is then

slowly transferred to the pipette. The spiral is kept glowing for about a minute after all the gas is in the pipette, and then the current is switched off. After allowing the pipette sufficient time to cool, the gas is transferred back to the burette. The carbon dioxide which has been formed, the volume of which is equal to the volume of methane originally present, is then absorbed in a potash pipette. As, however, the confining liquid in the Winkler combustion pipette is water, some carbon dioxide will have been dissolved, and the value obtained will be too low. It is therefore better not to calculate the amount of methane from the volume of carbon dioxide produced, but from the total contraction—i.e. the contraction after the combustion of the methane plus the contraction after absorbing the carbon dioxide. In this case it is immaterial that the water in the burette has dissolved carbon dioxide. In working with the Winkler explosion pipette, it is on no account permissible to transfer the whole of the gas into the pipette before passing the current through. Such a method of working would be liable to give rise to serious explosions, which might shatter the whole apparatus.

Example —

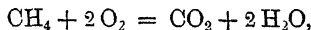
Gas measured	100.0	cu. cm.
After absorption with KOH	95.8	"
$\therefore \text{CO}_2 = 100 - 95.8 =$	4.2	"
After absorption with pyrogallol	92.4	"
$\therefore \text{O} = 95.8 - 92.4 =$	3.4	"
After absorption with Cu_2Cl_2	64.8	"
$\therefore \text{CO} = 92.4 - 64.8 =$	27.6	"
Non-absorbable residue	64.8	"
Residual gas measured	.	.	11.8	cu. cm.
Total volume after mixing with air	97.8	"
\therefore Air taken =	.	..	86.0	"
After combusting with Pd-asbestos	86.8	"
Contraction, $97.8 - 86.8 =$	11.0	"
$\therefore \text{H in 11.8 cu. cm., } \frac{2 \times 11.0}{3}$	7.3	"

H in total volume, $\frac{73 \times 648}{118}$. . .	40 1 cu. cm
After combusting in Winkler pipette and absorbing CO_2	. . .	79 0 "
Contraction, $86.8 - 79.0$. . .	7 8 "
\therefore Methane in 11.8 cu. cm, $\frac{7.8}{3}$		2 6 "
Methane in total volume, $\frac{26 \times 648}{118}$	14 3 "
Nitrogen, $64.8 - (40.1 + 14.3) =$	10 4 "

The gas therefore contains—

42	per cent	CO_2
34	"	O
27.6	"	CO
40.1	"	H
14.3	"	CH_4
10.4	"	N
<u>100.0</u>		

The union of methane with oxygen takes place according to the equation



1 volume methane + 2 volumes oxygen giving 1 volume carbon dioxide and 0 volume liquid water

The volume of carbon dioxide produced by the combustion is therefore equal to the volume of methane burnt. Also 3 volumes before combustion give 1 volume after combustion, the contraction, therefore, being 2 volumes. The volume of methane which was present is, therefore, $\frac{1}{2}$ the contraction. If the carbon dioxide produced in the combustion is removed by potash, the total contraction is 3 volumes, and in this case the volume of methane originally present is equal to $\frac{1}{3}$ of the total contraction.

If a mixture of hydrogen and methane is to be

analysed by burning both constituents simultaneously, the method of calculation is exactly the same as is set forth in Ex. 24, in the case of a mixture of hydrogen and carbon monoxide. The equations, of course, require to be altered accordingly

Ex. 23. - Analysis of a mixture of carbon dioxide, oxygen, carbon monoxide, hydrogen, and nitrogen (water gas).

Exactly 100 cu. cm. of water gas are measured in a Hempel burette, and the carbon dioxide absorbed by potash, oxygen by alkaline pyrogallol or alkaline hyposulphite solution, and carbon monoxide by two treatments with ammoniacal cuprous chloride.

The residual non-absorbable gas, consisting of hydrogen and nitrogen, is too much to be burnt, mixed with air, in one lot. The burette is, therefore, connected with a water pipette, and the gas passed over until only about 20-25 cu. cm. remain in the burette. The pipette is closed with a clip, and placed on one side as reserve supply in case the experiment should require to be repeated. The portion of gas remaining in the burette is then measured exactly, and mixed with air to give a total volume of rather less than 100 cu. cm. The mixture is now exploded exactly as described in Ex. 20, and the resulting diminution in volume measured.

Example.—

Gas measured	100.0 cu. cm.
After absorption with KOH	94.4 "
$\therefore \text{CO}_2 = 100 - 94.4 =$	5.6 "
After absorption with pyrogallol	92.2 "
$\therefore \text{O} = 94.4 - 92.2 =$	2.2 "
After absorption with Cu_2Cl_2	53.8 "
$\therefore \text{CO} = 92.2 - 53.8$	38.4 "
Non-absorbable residue	53.8 "

Volume of residual gas measured ...	20.2	cu. cm.
Total volume ...	96.4	"
∴ Air = 96.4 - 20.2 = ...	76.2	"
Volume after explosion ..	72.4	"
Contraction, 96.4 - 72.4 =	24.0	"
∴ Hydrogen in portion taken, $\frac{24.0 \times 2}{3}$ =	16.0	"
∴ Hydrogen in total volume, $\frac{16 \times 53.8}{20.2}$ =	42.6	"

53.8 cu. cm. non-absorbable gas contain 42.6 cu. cm. hydrogen

∴ nitrogen = 53.8 - 42.6 = 11.2 cu. cm.

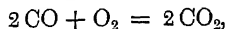
The water gas contains, therefore—

5.6	per cent	CO ₂
2.2	"	O
38.4	"	CO
42.6	"	H
11.2	"	N
<u>100.0</u>		

Ex 24.—Analysis of water gas by combustion of carbon monoxide and hydrogen.

In this method for the analysis of water gas, the residual gas after absorbing carbon dioxide and oxygen, consisting of carbon monoxide, hydrogen, and nitrogen, is mixed with oxygen and exploded. From the contraction in volume and the volume of carbon dioxide produced, the volumes of hydrogen and carbon monoxide originally present can easily be calculated.

The combination between carbon monoxide and oxygen takes place according to the equation



2 volumes carbon monoxide and 1 volume oxygen giving 2 volumes carbon dioxide.

The volume of carbon monoxide taken is thus equal to the volume of carbon dioxide produced. By deter-

analysed by burning both constituents simultaneously, the method of calculation is exactly the same as is set forth in Ex 24, in the case of a mixture of hydrogen and carbon monoxide. The equations, of course, require to be altered accordingly.

Ex. 23.—Analysis of a mixture of carbon dioxide, oxygen, carbon monoxide, hydrogen, and nitrogen (water gas).

Exactly 100 cu. cm. of water gas are measured in a Hempel burette, and the carbon dioxide absorbed by potash, oxygen by alkaline pyrogallol or alkaline hyposulphite solution, and carbon monoxide by two treatments with ammoniacal cuprous chloride.

The residual non-absorbable gas, consisting of hydrogen and nitrogen, is too much to be burnt, mixed with air, in one lot. The burette is, therefore, connected with a water pipette, and the gas passed over until only about 20–25 cu cm remain in the burette. The pipette is closed with a clip, and placed on one side as reserve supply in case the experiment should require to be repeated. The portion of gas remaining in the burette is then measured exactly, and mixed with air to give a total volume of rather less than 100 cu cm. The mixture is now exploded exactly as described in Ex. 20, and the resulting diminution in volume measured.

Example —

Gas measured	100.0	cu cm
After absorption with KOH	94.4	"
$\therefore \text{CO}_2 = 100 - 94.4 =$	5.6	"
After absorption with pyrogallol	92.2	"
$\therefore \text{O} = 94.4 - 92.2 =$	2.2	"
After absorption with Cu_2Cl_2	53.8	"
$\therefore \text{CO} = 92.2 - 53.8$	38.4	"
Non-absorbable residue	53.8	"

Volume of residual gas measured ...	20 2 cu. cm.
Total volume	96 4 „
∴ Air = 96 4 - 20 2 =	76 2 „
Volume after explosion	72 4 „
Contraction, 96 4 - 72 4 =	24 0 „
∴ Hydrogen in portion taken, $\frac{24 0 \times 2}{3}$ =	16 0 „
∴ Hydrogen in total volume, $\frac{16 \times 53 8}{20 2}$ =	42 6 „

53 8 cu. cm non-absorbable gas contain 42 6 cu. cm hydrogen

∴ nitrogen = 53 8 - 42 6 = 11 2 cu. cm

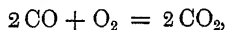
The water gas contains, therefore—

5 6	per cent	CO ₂
2 2	„	O
38 4	„	CO
42 6	„	H
11 2	„	N
<u>100 0</u>		

Ex. 24.—Analysis of water gas by combustion of carbon monoxide and hydrogen.

In this method for the analysis of water gas, the residual gas after absorbing carbon dioxide and oxygen, consisting of carbon monoxide, hydrogen, and nitrogen, is mixed with oxygen and exploded. From the contraction in volume and the volume of carbon dioxide produced, the volumes of hydrogen and carbon monoxide originally present can easily be calculated.

The combination between carbon monoxide and oxygen takes place according to the equation



2 volumes carbon monoxide and 1 volume oxygen giving 2 volumes carbon dioxide

The volume of carbon monoxide taken is thus equal to the volume of carbon dioxide produced. By deter-

mining the volume of carbon dioxide produced in the explosion, by absorbing with potash, the volume of carbon monoxide originally present is obtained. It is also apparent from the equation that the contraction after the explosion is equal to $\frac{1}{2}$ the volume of carbon monoxide originally present, or carbon dioxide produced. If, therefore, from the total contraction produced by exploding a mixture of hydrogen and carbon monoxide, the contraction due to carbon monoxide alone is subtracted, there is obtained the contraction due to hydrogen, and this on multiplying by $\frac{2}{3}$ gives the volume of hydrogen originally present.

In order to carry out the analysis 100 cu. cm. of gas are first measured, and the carbon dioxide and oxygen present measured by absorption. The major portion of the residual gas, consisting of carbon monoxide, hydrogen, and nitrogen, is transferred to a water pipette, so that only 20–25 cu. cm. remain in the burette. This is then mixed with air to give a total volume of about 100 cu. cm., and the mixture exploded in the explosion pipette. The hydrogen burns to water, and the carbon monoxide to carbon dioxide. The contraction in volume is measured, and the amount of carbon dioxide formed determined by absorbing with potash.

Example —

Gas measured	100.0 cu. cm.
After absorption with KOH	94.4 "
$\therefore \text{CO}_2 = 100 - 94.4 =$	5.6 "
After absorption with pyrogallol	92.2 "
$\therefore \text{O} = 94.4 - 92.2$	2.2 "
Residual gas measured	21.4 cu. cm.
Total volume	95.6 "
$\therefore \text{Air} = 95.6 - 21.4$	74.2 "
Volume after explosion	76.2 "
Contraction = $95.6 - 76.2$	19.4 "
After absorption with KOH	67.3 "
$\therefore \text{CO in residual gas taken, } 76.2 - 67.3 =$	8.9 "

$$\begin{aligned}
 \therefore \text{CO in total volume, } \frac{8.9 \times 92.2}{21.4} &= 38.4 \text{ cu cm} \\
 \text{Contraction due to CO (}\frac{1}{2}\text{ volume)} &4.5 \text{ ,,} \\
 \text{,, ,, H} = 19.4 - 4.5 &14.9 \text{ ,,} \\
 \therefore \text{H in residual gas taken, } \frac{14.9 \times 2}{3} &9.9 \text{ ,} \\
 \therefore \text{H in total volume, } \frac{9.9 \times 92.2}{21.4} &42.6 \text{ ,,}
 \end{aligned}$$

The non-absorbable gas therefore contains 42.6 cu cm H and 38.4 cu cm CO

$$\therefore \text{N} = 92.2 - (42.6 + 38.4) = 11.2 \text{ cu cm}$$

The gas contains, therefore—

56	per cent	CO ₂
22	"	O
38.4	"	CO
42.6	"	H
11.2	"	N
<hr/>		
100.0		
<hr/>		

Before returning the exploded gas from the explosion pipette to the burette, it is advisable to change the water in the latter, as this is liable to contain traces of alkali from the previous absorptions. This trace of alkali would absorb carbon dioxide from the exploded gas and lead to erroneous results.

Ex. 25.—Analysis of a mixture of O, CO, H, CH₄, and N by exploding the gas residue CO, H, CH₄, and N.

A mixture of CO, H, CH₄, and N can be analysed by mixing with air and exploding, then measuring the resulting contraction, the amount of carbon dioxide produced, and the excess of oxygen present in the exploded gas, this last value being obtained by again exploding with excess of hydrogen. From the data thus obtained, the proportion of the various constituents originally present may be calculated in the following manner—

Let x = volume of hydrogen
 y = volume of carbon monoxide
 z = volume of methane.
 O = volume of oxygen added
 N = volume of inert gas (nitrogen added + nitrogen originally present)¹

Then the volume of gas measured + volume of air added

$$V_1 = x + y + z + O + N$$

After the explosion the volume due to carbon monoxide and methane remains the same, for both these gases give an equal volume of carbon dioxide on combustion. The volume due to hydrogen disappears as the steam formed condenses to water. There also disappears the volume of oxygen required for the combustion of the carbon monoxide, hydrogen, and methane.

1 volume of hydrogen requires $\frac{1}{2}$ volume of oxygen to burn it, so the x volume present will require $\frac{x}{2}$ oxygen.

1 volume of carbon monoxide requires also $\frac{1}{2}$ volume of oxygen for complete combustion, so that $\frac{y}{2}$ volume of oxygen disappears when y volume is burnt.

Similarly, 1 volume methane requires 2 volumes oxygen, resulting in a contraction of $2z$ when this is burnt.

The amount of oxygen remaining after the explosion is therefore

$$O - \frac{x}{2} - \frac{y}{2} - 2z$$

The volume of exploded gas is thus

$$V_2 = N + y + z + \left(O - \frac{x}{2} - \frac{y}{2} - 2z\right).$$

¹ The method of *Classen*, somewhat modified, is here followed.

The carbon dioxide formed is then absorbed by potash, the diminution in volume being equal to the volume of the carbon monoxide and methane originally present.

After absorption with potash the volume is therefore

$$V_3 = N + \left(O - \frac{x}{2} - \frac{y}{2} - 2z\right).$$

To determine the amount of oxygen present, a known volume of hydrogen H is then added

The total volume, $V_4 = V_3 + H$, or, inserting the above value for V_3 ,

$$V_4 = N + \left(O - \frac{x}{2} - \frac{y}{2} - 2z\right) + H.$$

The volume V_4 is then exploded, when the oxygen present, $O - \frac{x}{2} - \frac{y}{2} - 2z$, disappears, together with twice this volume of hydrogen, $2\left(O - \frac{x}{2} - \frac{y}{2} - 2z\right)$

The volume after the explosion is therefore

$$V_5 = N + H - 2\left(O - \frac{x}{2} - \frac{y}{2} - 2z\right).$$

In order to obtain values for x , y , and z from these five equations, they must first be brought together into three equations. After carrying across the values for O and H to the left-hand side, we get:

- (1) $V_1 - O = N + x + y + z$
- (2) $V_2 - O = N - \frac{x}{2} + \frac{y}{2} - z$
- (3) $V_3 - O = N - \frac{x}{2} - \frac{y}{2} - 2z.$
- (4) $V_4 - O - H = N - \frac{x}{2} - \frac{y}{2} - 2z$
- (5) $V_5 + 2O - H = N + x + y + 4z$

Subtracting equation (2) from equation (1), equation (3)

from equation (2), and equation (5) from equation (4), we get

$$(6) \quad V_1 - V_2 = \frac{3x}{2} + \frac{y}{2} + 2z.$$

$$(7) \quad V_2 - V_3 = y + z$$

$$V_4 - V_5 - 3O = -\frac{3x}{2} - \frac{3y}{2} - 6z.$$

or dividing by 3.

$$(8) \quad \frac{V_4 - V_5 - 3O}{3} = -\frac{x}{2} - \frac{y}{2} - 2z.$$

Adding together equations (6) and (8), we obtain:

$$x = V_1 - V_2 + \frac{V_4 - V_5 - 3O}{3}.$$

To obtain the value for y , this value for x , together with the value $z = V_2 - V_3 - y$ obtained from equation (7), are substituted in equation (6), giving:

$$V_1 - V_2 = \frac{3}{2} \left(V_1 - V_2 + \frac{V_4 - V_5 - 3O}{3} \right) + \frac{y}{2} + 2(V_2 - V_3 - y),$$

whence

$$y = \frac{1}{3} [V_1 - V_2 + 4(V_2 - V_3) + V_4 - V_5 - 3O]$$

The value of z may be obtained from equation (7).

$$z = V_2 - V_3 - y,$$

or by substituting the above value for y

$$\begin{aligned} z &= \frac{1}{3} [-(V_1 - V_2) - (V_2 - V_3) - (V_4 - V_5 - 3O)] \\ &= \frac{V_3 + V_5 + 3O - (V_1 + V_4)}{3}. \end{aligned}$$

The amount of nitrogen is given by the difference between the volume of gas measured and the sum of x , y , and z .

In order to carry out the analysis, 100 cu cm of the gas mixture are first measured, and the amount of carbon

dioxide and oxygen measured by absorption in the usual manner. 15-20 cu cm of the residual gas are then measured, mixed with air to nearly 100 cu. cm. and exploded. The resulting contraction is measured, and the carbon dioxide formed determined. A measured volume of hydrogen is then added, the mixture exploded, and the contraction again measured. It may happen that the mixture, after adding the hydrogen, will not explode, in this case a sufficient volume of electrolytic gas should be added to bring about an explosion. It is not necessary to measure the volume of the explosive gas added, as it disappears completely after explosion.

Example —

Volume measured	100.0	cu cm	
After absorption with KOH	95.8	"	
∴ CO ₂ = 100 - 95.8	4.2	"	
After absorption with pyrogallol	92.4	"	
∴ O = 95.8 - 92.4	3.4	"	
Non-absorbable residue	92.4	"	
Gas residue measured	20.4	cu cm.	
Total volume	96.6	"	= V ₁
∴ Air	76.2	"	
Containing oxygen	15.93	"	
" nitrogen	60.27	"	
Volume after first explosion	73.8	"	= V ₂
After absorption with KOH	64.5	"	= V ₃
Hydrogen added	10.2	"	
Total volume	74.7	"	= V ₄
After explosion	68.7	"	= V ₅

$$H = \left(V_1 - V_2 + \frac{V_4 - V_5 - 3O}{3} \right)$$

$$= 96.6 - 73.8 + \frac{74.7 - 68.7 - 47.79}{3}$$

$$= 8.9 \text{ cu. cm. in } 20.4 \text{ cu cm.}$$

$$CO = \frac{1}{3}[V_1 - V_2 + 4(V_2 - V_3) + V_4 - V_5 - 3O]$$

$$= \frac{1}{3}[96.6 - 73.8 + 4(73.8 - 64.5) + 74.7 - 68.7 - 47.79]$$

$$= 6.1 \text{ cu. cm. in } 20.4 \text{ cu cm.}$$

$$\text{CH}_4 = \frac{V_3 + V_5 + 3\text{O} - (V_1 + V_4)}{3}$$

$$= \frac{64.5 + 68.7 + 47.8 - 96.6 - 74.7}{3}$$

$$= 3.2 \text{ cu cm in } 20.4 \text{ cu cm}$$

$$\text{N} = 20.4 - (8.9 + 6.1 + 3.2) = 2.2 \text{ cu cm in } 20.4 \text{ cu cm}$$

The gas therefore contains—

4.2	per cent	CO ₂
3.4	„	O
40.3	„	H
27.6	„	CO
14.5	„	CH ₄
10.0	„	N
<hr/>		
100.0		

Ex. 26.—Determination of the amount and composition of the gases dissolved in water according to the method of *Preusse* and *Tiemann*.

The apparatus necessary for this experiment is shown in fig. 19. It consists of two boiling flasks A and B, each of about 1 l. capacity, and a gas collector C. This has a diameter of about 35 mm and a height of 300 mm., and is drawn out to a capillary tube fitted with a short piece of thick-walled rubber tubing and a pinchcock *m*. A is closed by a one-hole rubber stopper, through which passes a bent glass tube *a*, ending flush with the stopper. C is closed by a two-holed rubber stopper, with two glass tubes bent at right angles, one tube *e* projecting about 8 cm into the vessel, the other *f* ending just above the stopper. The flask A is connected to the gas collector by the bent tube *cd*, the necessary joints being made with thick-walled rubber tubing, the connection *b* carrying a pinchcock. B is closed with a two-holed rubber stopper with two bent glass tubes, one of which *i* reaches almost to the bottom of the flask, and the other *k* ending

just below the stopper. Attached to *k* is a length of rubber tubing *l*. B is connected to the gas collector by the bent tube *gh*. To use the apparatus, the capacity of A must first be determined. To do this the rubber stopper with glass tube is pushed into the flask as far as possible, and the position of the lower edge of the stopper marked. The stopper is then removed, and the flask filled up to this mark with water, using first measuring

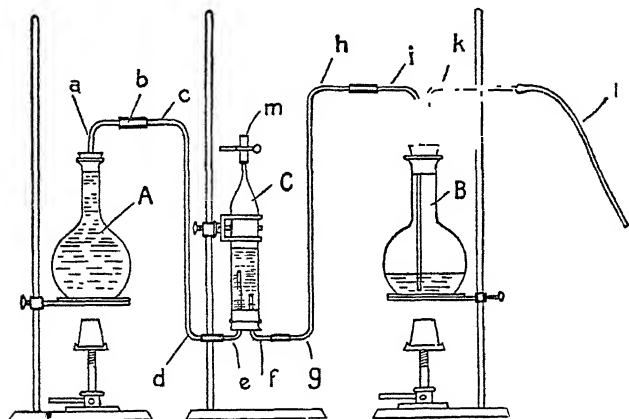


Fig 19

flasks, then a burette. The volume of water required gives the capacity of the flask. The flask B is then filled with a 5-per-cent solution of caustic potash, and the gas collector, together with all connecting tubes up to the connection *b*, filled with this solution by blowing through the tubing *l*, and opening the pinchcocks *b* and *m*. Dilute caustic potash is used for this purpose, so that the carbon dioxide which all ordinary waters contain may be absorbed, as it is not required to estimate this gas in this case. The flask A is then completely filled with water, and the rubber stopper pushed in, so that

the displaced water completely fills the tube *a*, which is then connected to *c*, and the pinchcock at *b* removed.

The two flasks are then heated, so that the contents of *B* boil gently, and of *A* rather more vigorously. The air dissolved in the water is driven out, and collects in the upper part of the gas collector. Steam also enters the gas collector, heats the caustic solution, and drives out all dissolved air. The air driven out is removed from time to time by opening the pinchcock *m*, and blowing through the tube *l*.

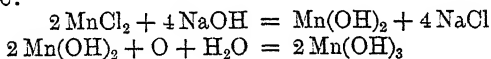
When air bubbles no longer collect in the gas collector the tube *b* is closed, the burner under *A* extinguished, and the flask removed. The apparatus is now ready for the actual experiment, as all dissolved air has been removed from the potash solution, and as *b* and *m* are closed, and the contents of *B* kept gently boiling, no air can enter.

The flask *A* is then filled with the water to be investigated, the stopper pushed in so as to fill the glass tube with the displaced water, and the tube then attached to the rest of the apparatus at *b*. Care must be taken that no air bubble remains below the stopper or in the various connections. The pinchcock is then removed, and the water in *A* heated to boiling. The dissolved gas is gradually driven out of the water and collects in the gas collector. Care must be taken that the water does not boil so vigorously as allow air bubbles to escape through *f*, *g*, *h*. After boiling for 20 min. the flame is extinguished, and it is noted whether the water drawn back completely fills flask *A*, or whether small air bubbles collect below the stopper. In this latter case the boiling is continued until these are displaced. The flame under *A* is then removed, *b* closed, and the flask removed. The short rubber connection at *m* is then filled with water, a capillary connection tube inserted, this connected to a

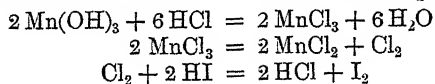
Hempel burette, and the gas transferred and measured. After measuring the volume of the gas, it is mixed with excess of hydrogen, exploded in the explosion pipette, transferred back to the burette, and the contraction measured. From the contraction observed the amount of oxygen present is readily calculated, and the residue is put down as nitrogen.

Ex. 27.—Determination of the amount of oxygen dissolved in water by *L. W. Winkler's* volumetric method.

In this method a measured volume of the water to be examined is brought into intimate contact, in absence of air, with a solution of caustic soda containing potassium iodide, and a solution of a manganous salt. The latter reacts with the alkali, giving a precipitate of manganous hydroxide, which immediately combines with the oxygen dissolved in the water to give manganic hydroxide:



If, hydrochloric acid is now added to the reaction mixture, the manganic hydroxide dissolves to form manganic chloride, which then splits up into manganous chloride and free chlorine. This latter then liberates an equivalent amount of iodine from the potassium iodide, or rather hydriodic acid present, and this can be titrated against a standard solution of sodium thiosulphate.



From the equations it is seen that 1 molecule iodine corresponds to $\frac{1}{2}$ molecule oxygen.

The reagents necessary for carrying out the experiment are—

1 *A solution of potassium iodide in caustic soda*—10 g potassium iodide are dissolved in 100 cu. cm. 33-per-cent caustic soda solution, the soda being preferably prepared from the metal. The potassium iodide used must be free from iodate, and the soda from nitrite. The mixture after acidifying must give no blue coloration with starch paste.

2 *A solution of manganous chloride*—80 g crystallized manganous chloride, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, are dissolved in 100 cu. cm. water. The solution must be free from iron, and must give no blue coloration when acidified and mixed with a solution of potassium iodide and starch paste.

3 *Pure concentrated hydrochloric acid containing no free chlorine*

The analysis is carried out in a glass bottle of about 250 cu. cm. capacity, provided with a well-ground-in glass stopper. The capacity is measured by weighing the dry bottle and stopper to 1 g, then filling completely with distilled water, inserting the stopper so that no air bubbles are enclosed, and weighing again after well drying the outside.

The difference between the two weights gives the capacity of the bottle.

The bottle is then completely filled with the water to be investigated, and by the aid of a long-stemmed pipette, first 1 cu. cm. alkaline potassium iodide, and then 1 cu. cm. of manganous chloride solution are run on to the bottom of the bottle. The water displaced by the reagents is allowed for in the calculation. The stopper is then inserted, taking care not to enclose air bubbles, and the reagents intimately mixed with the water by repeatedly inverting the bottle. The whole is then allowed to stand quietly until the precipitate has settled to the bottom.

When this has taken place, the stopper is removed

and 3 cu cm concentrated hydrochloric acid is run on to the bottom of the bottle with a long-stemmed pipette, the stopper replaced, and the bottle shaken. The water displaced by the acid need not be taken into account, as the whole of the oxygen originally present in the water will now be combined with the manganese.

The contents of the bottle are then washed out into an Erlenmeyer flask, and the liberated iodine titrated against N/100 sodium thiosulphate.

Example—

Weight of bottle filled with water	604.4 g
„ empty bottle	342.2 „
Capacity of bottle . . .	262.2 „
Volume occupied by reagents . . .	20 „
„ of water analysed . . .	260.2 „
N/100 thiosulphate required	27.6 cu cm.
1 cu cm thiosulphate is equivalent to	0.00008 g O
27.6 cu cm „ are „	0.002208 „ O
Weight of 1 l oxygen	1.42923 „

$$\therefore 0.002208 \text{ g O} = \frac{1000 \times 0.002208}{1.42923} = 1.55 \text{ cu cm O}$$

\therefore 260.2 cu cm of the water analysed contain 1.55 cu cm oxygen at 0° and 760 mm

$$\therefore 1 \text{ l of water contains } \frac{1.55 \times 1000}{260.2} = 5.94 \text{ cu cm oxygen at } 0^\circ \text{ and } 760 \text{ mm}$$

Ex. 28.—Analysis of illuminating (coal) gas with the Hempel apparatus.

Purified coal gas is essentially a mixture of the following gases:—

Carbon dioxide
Heavy hydrocarbons.
Oxygen.
Carbon monoxide.
Hydrogen
Methane.
Nitrogen

To carry out the analysis, water saturated with coal gas must first be prepared. This is readily done by placing 1 l of water in a 2-l flask, displacing the air by coal gas, closing the flask with a rubber stopper, and shaking vigorously for some time. This should be repeated once again with the same liquid and fresh gas. 100 cu. cm. of coal gas are then measured over this solution, the carbon dioxide absorbed by potash, then heavy hydrocarbons by bromine water, oxygen by alkaline pyrogallol, and carbon monoxide by two treatments with cuprous chloride solution. The non-absorbable residue, consisting of hydrogen, methane, and nitrogen, is then transferred to a water pipette, and the liquid in the burette substituted by distilled water. 10 to 15 cu. cm. of the gas residue are then measured off, mixed with air to nearly 100 cu. cm., and exploded in the explosion pipette. The contraction produced is then measured, the carbon dioxide formed in the explosion absorbed, and finally the excess of oxygen determined by a pyrogallol pipette. The excess of oxygen is measured simply to show whether sufficient of this gas has been present for the complete combustion of the hydrogen and methane.

Example —

Gas measured	100.0 cu. cm.
After absorption with KOH	97.4 "
∴ CO ₂ = 100 - 97.4	.	.	.	2.6 "
After absorption with bromine water				92.6 "
∴ Heavy hydrocarbons, 97.4 - 92.6				4.8 "
After absorption with pyrogallol ..				92.0 "
∴ Oxygen, 92.6 - 92.0	.	.	.	0.6 "
After absorption with cuprous chloride				80.9 "
∴ CO = 92.0 - 80.9...	.	.	.	11.1 "
Non-absorbable residue	80.9 "
Residual gas measured	15.0 cu. cm.
Total volume...	98.6 "
∴ Air	83.6 "

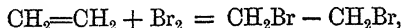
Volume after explosion	75.6 cu. cm
Contraction, 98.6 — 75.6	23.0 „
After absorption of KOH	70.6 „
∴ Methane in gas residue measured,		
75.6 — 70.6 =	5.0 „
Methane in total volume	27.0 „
Contraction due to methane	10.0 „
∴ Contraction due to hydrogen,		
23.0 — 10.0 =	13.0 „
∴ H in gas residue measured, $\frac{13.0 \times 2}{3}$	8.7 „
H in total volume	46.9 „
N = (80.9) — (27.0 + 46.9)	7.0 „

The sample of coal gas contains, therefore—

2.6	per cent carbon dioxide
4.8	„ heavy hydrocarbons
0.6	„ oxygen
11.1	„ carbon monoxide
27.0	„ methane
46.9	„ hydrogen
7.0	„ nitrogen
<u>100.0</u>	

Ex. 29.—Estimation of ethylene and benzene in coal gas according to *Haber* and *Oechelhauser*.

If bromine water be allowed to react with a gas containing ethylene and benzene, both of these substances are absorbed, and from the resulting contraction the combined volume of the two is obtained. The ethylene present combines chemically with the bromine, giving ethylene dibromide, according to the equation



whilst benzene is not attacked but only mechanically removed. There is, therefore, used up only that amount of bromine corresponding with the amount of ethylene present, and this amount can be determined by titrating

the bromine water before and after absorption of the gas, against standard thiosulphate

The difference between the amount of ethylene thus found and the total amount of ethylene and benzene, gives the amount of the latter.

To perform the analysis the Bunte burette is used. 90 cu cm. of coal gas are measured over coal-gas water, the temperature and barometric pressure being noted

The water up to the tap is then removed by suction, the burette allowed to drain 5 min, and the drainage removed. About 35 cu cm half-saturated bromine water is then poured into a small porcelain basin, and about 10-15 cu cm of this allowed to ascend into the burette. The height of the bromine water is read off, and then a little water passed in to rinse out the capillary. The burette is now shaken vigorously for 2 min, so that all heavy hydrocarbons are absorbed, care being taken that excess of bromine remains present. A sufficient quantity of 20-per-cent potassium iodide solution is now allowed to enter, and after shaking and then adjusting the pressure the volume is read off. The whole of the contents of the burette is next washed out into an Erlenmeyer flask, and the liberated iodine titrated against sodium thiosulphate.

The experiment is now repeated with the same burette and bromine water, but substituting air for the coal gas previously used, the bromine water being allowed to rise to exactly the same height in the burette as in the first experiment. The difference between the amounts of thiosulphate required in the two experiments gives the amount of ethylene present.

Example —

Height of liquid at commencement	..	100 cu. cm
∴ Volume measured	.	900 "
$t = 20^{\circ}$, Bar. = 755 mm,		

Height of bromine water	40 cu. cm.
„ liquid after admitting KI solution and adjusting pressure		145 „
∴ Heavy hydrocarbons =	145 — 100	45 „
	=	50 per cent

Blank experiment requires	. 1420 cu cm	N/10 thiosulphate
Actual „ with coal gas	1110 „	„ „ „
Difference	31	„ „ „

310 cu cm. N/10 thiosulphate correspond to 0.04346 g ethylene = 3.45 cu cm ethylene at 0° and 760 mm = 3.82 cu cm. moist ethylene at 20° and 755 mm

90 cu cm of coal gas contain 3.82 cu cm = 4.24 per cent ethylene

Total heavy hydrocarbons	...	5.00 per cent
Ethylene	...	4.24 „
Benzene (by difference)	..	. 0.76 „

Ex. 30.—Determination of the amount of oxygen in the air by means of *Wohl's* gas flask.

The principle of this method is as follows —

The gas is enclosed in a flask of known capacity, and treated in the flask with a suitable absorption reagent. Water is then allowed to enter the flask until the residual gas is under its original pressure. The volume of the constituent absorbed is then equal to the volume of absorption reagent plus the volume of water which has entered. The flask used is an ordinary boiling flask of about 100–200 cu cm capacity. It is closed with a rubber stopper with one hole, which can be forced in to a mark running round the neck of the flask about 1½–2 cm from the lip. A capillary tube, 4 cm. long, passes through the stopper, and attached to this is a short length of thick-walled pressure tubing provided with a pinchcock (fig 20)

To measure the capacity of the flask, it is first rinsed with distilled water, allowed to drain about a minute,

and then either 100 or 200 cu. cm. water run in, according to the size of the flask, from a 100-cu.-cm. pipette. The flask is then filled exactly to the mark from a burette. To carry out the analysis, a funnel, having a stem cut off straight, about 3-4 cm. long is inserted into the rubber tube, the stopper is then forced into the flask exactly to the mark, and the pinchcock closed.

10 cu. cm. of alkaline sodium hyposulphite solution are then poured into the funnel, and any air bubbles which may remain in the rubber tube detached with a wire.

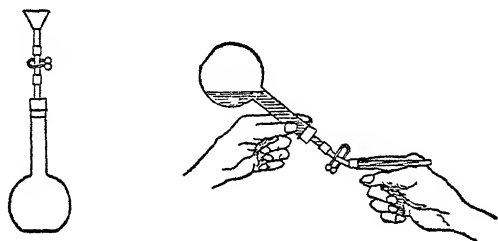


Fig 20

On cautiously opening the pinchcock a few drops of the reagent enter the flask, and absorption of oxygen begins. This can be accelerated somewhat by gently agitating the flask. As the absorption proceeds more reagent is allowed to enter, always keeping the funnel filled with liquid. When all the reagent possible has entered, the flask is held with the thumb and forefinger in such a way that the funnel lies to the back of the hand, and vigorously shaken for 3 min. The funnel is then filled up with distilled water, and this allowed to run into the flask till no more will enter, care being taken that no air bubbles pass in.

In order to bring the flask and contents to its original temperature, it is immersed for 1-2 min. in a bath of

water at room temperature, and the pinchcock opened, when more water will enter. To make quite sure that the flask is cooled to the right temperature it must again be immersed in the bath, and the pinchcock then cautiously opened. No more water should enter, if it does, the operation must be repeated. The gas in the flask is, however, under a pressure greater than atmospheric pressure, being, in fact, under a pressure equal to the atmospheric pressure plus the pressure of the column of water in the capillary tube, rubber connection, and funnel.

To reduce to atmospheric pressure, the funnel is first removed and substituted by a short length of glass tubing. The flask is then held in the position shown in the figure, so that the neck is filled with liquid, and the pinchcock squeezed. The short length of tube then fills with water, and a little is forced out. The flask is then very carefully lowered, keeping the pinchcock open, until it is exactly horizontal. Water then flows back from the tube into the flask until the pressure inside is exactly equal to the atmosphere. The pinchcock is then closed, and removed, together with the stopper. There is now in the flask a volume of liquid equal to the volume of oxygen absorbed.

To measure this volume, 50 or 100 cu. cm. of water are run in (according to size of flask) from a pipette, and the flask then filled exactly to the mark from a burette. The difference between the capacity of the flask and the volume now required to fill it, is equal to the volume of liquid already in the flask, i.e. to the volume of absorbed oxygen.

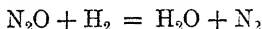
In pushing in the stopper and in reducing to atmospheric pressure, the greatest possible care must be taken not to touch the body of the flask with the hand.

Example.—

Capacity of flask	174.5 cu. cm.
Volume required to fill up	.		138.3 "
∴ O in 174.5 cu. cm	=	174.5 - 138.3 =	36.2 "
∴ O volume per cent	=	$\frac{36.2 \times 100}{174.5}$	= 20.74 "

Ex. 31.—Estimation of nitrous oxide.

If a mixture of nitrous oxide and hydrogen be heated to a sufficiently high temperature, the hydrogen burns at the expense of the nitrous oxide, producing water and nitrogen



1 vol nitrous oxide + 1 vol hydrogen giving 1 vol nitrogen + 0 vol water. The contraction produced is thus equal to the volume of nitrous oxide originally present. The gas mixture can either be exploded with an electric spark, or better, combination brought about without explosion by passing the mixture through a glowing *Drehschmidt* platinum capillary.

The *Drehschmidt* platinum capillary is a thin platinum tube, to the ends of which are soldered two copper tubes bent at right angles. To prevent the joints from becoming too hot they are protected by copper jackets filled with water.

In exact analyses, it is necessary to know the exact volume content of the platinum capillary for the following reason:—The capillary contains at the commencement of the experiment a mixture of oxygen and nitrogen (air) during the combination of the nitrous oxide and hydrogen, this oxygen combines with an equivalent amount of hydrogen to form water, and, therefore, there disappears, not only this volume of oxygen, but the hydrogen necessary for its combustion, and this requires to be corrected for. To measure the capacity of the platinum capillary the following method is adopted.

One end of the capillary is connected to a Hempel burette containing mercury then by raising the levelling tube the level of the mercury is brought to the zero mark, and the free end of the capillary closed by a rubber tube

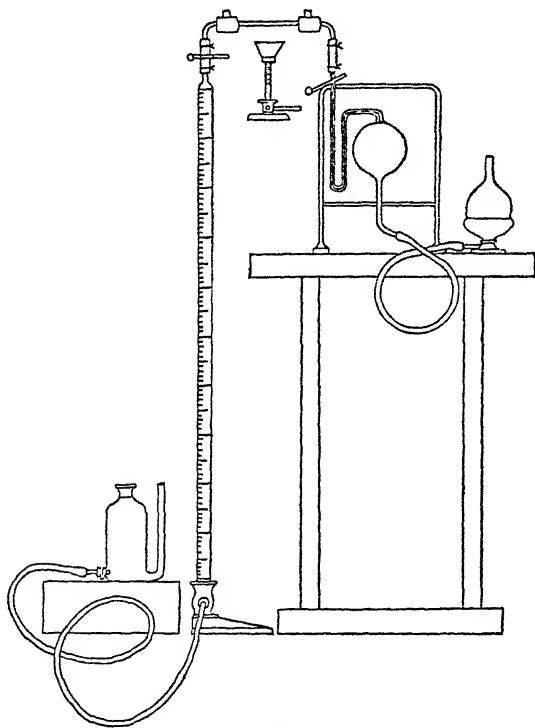


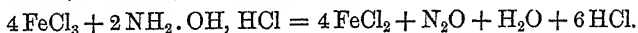
Fig. 21

and clip. The levelling tube is then lowered until the distance between the mercury surfaces in the measuring and levelling tubes is equal to half the prevailing barometric height. The volume of the air in the capillary is thus doubled, so that the volume as read off in the burette is equal to the internal capacity of the capillary.

As nitrous oxide is very appreciably soluble in water, it must be measured over mercury. The burette used is an ordinary Hempel burette, the levelling tube of which is replaced by a levelling vessel of the form shown in the diagram (fig 21), the mercury in the narrow side tube of which can readily be brought to the same height as the mercury in the measuring tube.

To carry out the analysis, about 20 cu cm of nitrous oxide are accurately measured, and mixed with about 30 cu cm. of hydrogen. The Drehschmidt capillary is then connected to a mercury pipette by a short piece of pressure tubing, and the connection closed with a pinchcock. The other end of the capillary is connected with the burette, the pinchcock of the pipette opened, and the height of the mercury in the pipette capillary marked. The platinum tube is now heated with a small flat burner, the levelling vessel of the burette raised and that of the pipette lowered, and the pinchcock carefully opened so that the gas passes through the heated tube in a slow stream until only about $\frac{1}{2}$ cu. cm remains in the burette. The gas is then returned to the burette, and the operation once more repeated. After waiting about fifteen minutes, so that the gas may cool completely, the mercury in the pipette capillary is adjusted to its former level, and the volume of the gas then read off.

The nitrous oxide is obtained either from a bomb or by the action of hydroxylamine hydrochloride on a solution of ferrous chloride, according to the equation:



A boiling flask of about 250 cu. cm capacity is filled about one-third full with a concentrated solution of ferrous chloride, and fitted with a two-hole rubber stopper, through one hole of which passes a dropping funnel and through the other a gas delivery tube.

The solution in the flask is heated to 50-70°, and the hydroxylamine hydrochloride solution dropped in through the funnel,

when the nitrous oxide is immediately evolved. Before taking a sample of gas for the experiment, the gas must be allowed to escape from the apparatus until all air is displaced.

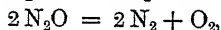
• The mercury pipette (see fig. 21) consists of two bulbs, containing mercury one of which is mounted on an iron stand and ends in a capillary with several bends, as in the Hempel pipette. This bulb is connected by a length of thick-walled rubber tubing to the second bulb, the levelling bulb, which is mounted on an iron foot.

Calculation of result—Internal capacity of platinum capillary = 1.6 cu. cm. This volume of air contains 33 cu. cm. oxygen, which requires 66 cu. cm. hydrogen for complete combustion. There disappears, therefore, 99 cu. cm. of gas due to the air in the capillary tube, in addition to the contraction due to the actual combination of nitrous oxide and hydrogen. This amount must consequently be subtracted from the total contraction to obtain the contraction due to the combustion of nitrous oxide alone, which, according to the equation, is equal to the volume of nitrous oxide originally present.

Example—

Volume of N_2O measured	..	19.8	cu. cm.
Total volume	.	50.4	"
∴ Hydrogen = $50.4 - 19.8$		30.6	"
Volume after combustion		29.9	"
Contraction, $50.4 - 29.9$.	20.5	"
Contraction due to N_2O = $20.5 - 0.99$.	19.5	"
∴ Volume of N_2O	.	19.5	"

Lunge has proposed to absorb nitrous oxide in air-free alcohol. This method, however, does not give accurate results, as other gases are very appreciably soluble in alcohol. Another method for the estimation of nitrous oxide depends on the fact that when this gas is heated to a sufficiently high temperature it splits up into nitrogen and oxygen according to the equation

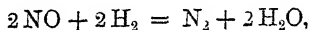


2 volumes of nitrous oxide giving 2 volumes of nitro-

gen and 1 volume of oxygen. The increase in volume is thus equal to half the volume of nitrous oxide originally present. *Winkler* proposed to bring about this reaction by passing the gas over a glowing palladium wire, but in this form the method is inaccurate. *Hempel* has more recently worked at this method, and brings about the dissociation of the gas into its components, nitrogen and oxygen, by mixing with explosive electrolytic oxygen-hydrogen mixture (detonating gas), and exploding the whole. The high temperature of the explosion causes the gas to dissociate.

The combustion with hydrogen is, however, the more preferable method, as in this case the change in volume is equal to the volume of nitrous oxide originally present, whilst in the dissociation method the change is only equal to one-half.

Nitric oxide may be estimated in exactly the same way as nitrous oxide, the reaction proceeding according to the equation



2 volumes nitric oxide + 2 volumes hydrogen giving 1 volume nitrogen. The contraction produced by exploding 2 volumes of nitric oxide is thus 3 volumes, so that the amount of nitric oxide originally present is equal to two-thirds of the contraction. In carrying out this estimation the mixture of nitric oxide and hydrogen must be passed as slowly as possible through the platinum capillary, which must be heated to bright redness, otherwise part of the nitric oxide is reduced to ammonia, and too high a result obtained.

Ex. 32.—Qualitative tests for carbon monoxide.

Hæmoglobin, the colouring matter of blood, has the property of combining with oxygen to form a body

called oxyhæmoglobin. Hæmoglobin is contained in venous, oxyhæmoglobin in arterial blood. If carbon monoxide be allowed to react with a solution of hæmoglobin or oxyhæmoglobin, it combines with the former to give carbon-monoxide hæmoglobin, or displaces oxygen from the latter to form the same compound.

Carbon-monoxide hæmoglobin gives quite different reactions to hæmoglobin or to oxyhæmoglobin, so that by using blood even traces of carbon monoxide may be detected.

Preparation of carbon-monoxide blood—To prepare this for the experiments which are described below, about 50 cu. cm. defibrinated blood are placed in a flask of about 200 cu. cm. capacity, and the air displaced by coal gas. The flask is closed with a stopper and vigorously shaken, the gas being replaced by fresh gas three or four times, and the shaking repeated. By this treatment the oxyhæmoglobin is converted into carbon-monoxide hæmoglobin.

Hoppe-Seyler's caustic soda test—10 cu. cm. of carbon-monoxide blood are placed in a test tube, side by side with 10 cu. cm. ordinary blood, and 10 cu. cm. of caustic soda solution of sp. gr. 1.3 added to both. The normal blood gives an almost black, slimy precipitate, whilst the carbon-monoxide blood coagulates to a bright-red mass.

Hoppe-Seyler's test is the oldest of the various tests which have been proposed to detect carbon monoxide in blood, and it has been of great service in the case of suspected carbon-monoxide poisoning. The test is, however, not very delicate, and fails when the blood to be examined contains less than 1 part of carbon-monoxide blood in 5 parts normal blood.

The potassium ferrocyanide test of Kunkel and Welzel.—5 cu. cm. carbon-monoxide blood and 5 cu. cm.

normal blood are diluted side by side with 20 cu cm water. To each of these dilute solutions, contained in a test tube, are added 5 cu. cm 20-per-cent potassium ferrocyanide solution, and then 1 cu cm acetic acid (1 volume glacial acetic acid + 2 volumes water), and the contents of the tubes gently mixed. A precipitate is thus obtained which in the case of normal blood is grey, but a bright cherry-red with the blood containing carbon monoxide. The test is very delicate, as it is quite possible to detect the difference in colour between normal blood and blood containing only 1 part in 12 of carbon-monoxide blood. After 2 to 6 days the difference in colour of the two precipitates disappears.

The presence of carbon monoxide in tobacco smoke may readily be demonstrated by means of this test. 20 cu cm. diluted blood is placed in a flask of about 200 cu cm. capacity, provided with a two-holed stopper, through one hole of which passes a glass tube bent at right angles reaching nearly to the bottom of the flask, the other hole remaining open. Tobacco smoke is blown several times through the glass tube, and the flask well shaken. On testing 10 cu. cm. of the blood, it will be found that the colour reaction is quite distinctly noticeable.

Kunkel and Welzel's tannin test—5 cu cm of each of the two diluted blood solutions as prepared for the ferrocyanide test are placed in test tubes, and about 15 cu cm. of 1-per-cent solution of tannin added.

At first sight the two solutions appear to be of the same shade of red, but on examining carefully it will be seen that the carbon-monoxide blood tube shows a distinct bluish shade, whilst the normal blood is inclined to yellow. After standing some time, the difference in shade becomes more pronounced. The precipitate obtained with normal blood becomes slowly brownish, then brownish-grey, and finally after 24 to 48 hr grey, whilst

the precipitate from carbon-monoxide blood retains its bright carmine colour.

The tannin test is about as sensitive as the ferrocyanide test, but has the great advantage that the difference in the two colours is extraordinarily stable, even in open test tubes. After ten months the difference in colour between the two precipitates is distinctly noticeable. The sensitiveness and great stability of this test make it a very valuable one for forensic purposes.

Besides the tests mentioned, an extraordinarily large number of others have been described, but none of these have the sensitiveness of the potassium ferrocyanide and tannin reactions.

Detection of carbon monoxide by spectroscopic methods
—Carbon-monoxide blood has a brighter colour than normal blood. The difference in colour is not, however, readily noticeable to the naked eye, but is readily shown by the spectroscope. To demonstrate the difference, normal blood is diluted with 40 times its volume of water, so that the solution is only a faint rose colour. It is then placed in a small glass trough with parallel walls, between the slit of a spectroscope and a source of light. On looking through the instrument, two broad absorption bands are noticeable. Two or three drops of ammonium sulphide are now added to the contents of the trough, and after stirring, the solution again examined through the spectroscope. It will be seen that a single but distinctly broader band has taken the place of the two bands first observed.

If the solution of normal blood be now replaced by a solution of carbon-monoxide blood of similar dilution and observed through the spectroscope, two absorption bands are also seen, almost in the same position as with normal blood, though actually displaced a little towards the green end.

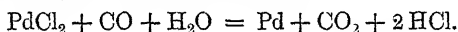
On mixing with ammonium sulphide, however, the two bands do not disappear but remain unaltered

This reaction is so characteristic that a confusion with any other gas which may be dissolved in blood is out of the question. The spectroscopic method is not, however, so delicate as the purely chemical tests

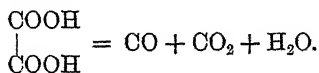
If it is required to test for the presence of small quantities of carbon monoxide, e.g. in air, by any one of these methods, which might be of great hygienic importance, the following method of procedure can be adopted. A large flask of about 10 l capacity is filled with distilled water, and then emptied in the air it is required to test. Normal blood, diluted as described, is then poured into the flask and shaken vigorously for some time. The blood absorbs any carbon monoxide which may be present, and can then be tested either spectroscopically or chemically for the presence of this gas.

Using the tannin test, it is possible to show the presence of carbon monoxide in air containing as little as 0.023 per cent of this gas.

Detection by means of palladious chloride—If carbon monoxide be passed into an aqueous solution of palladious chloride, it is oxidized to carbon dioxide, and at the same time metallic palladium is precipitated.



To obtain a stream of carbon monoxide, a few grammes of oxalic acid are heated with a little concentrated sulphuric acid in a test tube provided with a bored cork and bent glass delivery tube. A mixture of equal volumes of carbon monoxide and carbon dioxide is obtained, according to the equation:



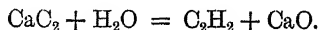
If a current of gas so obtained be led into a solution of sodium-palladious chloride contained in a test tube, a black precipitate of metallic palladium is at once obtained, and the brownish-red solution is decolorized. This test for carbon monoxide is very delicate, but has the great disadvantage that it is not confined to carbon monoxide, as other gases, e.g. hydrogen and ethylene, are also able to reduce palladious chloride.

Ex. 33.—Qualitative tests for acetylene.

Acetylene, C_2H_2 or $CH\equiv CH$, possesses the property of giving very characteristic precipitates with ammoniacal solutions of copper or silver salts. With ammoniacal cuprous chloride, for example, it gives a fine red body, copper acetylide, C_2H_2 , Cu_2O , which when dry is extraordinarily explosive, and with ammoniacal silver solutions, silver acetylide, C_2H_2 , Ag_2O , which is also highly explosive when dry. The two compounds are insoluble in water and in ammonia, and may be used to detect even traces of acetylene.

Copper test—1 g of crystallized copper sulphate is dissolved in a 50-cu-cm flask in as little water as possible, and 4 cu cm 20-per-cent ammonia added. A concentrated aqueous solution containing 3 g of hydroxylamine hydrochloride is added to this deep-blue liquid, when gas evolution begins, and the solution is decolorized with the formation of a cuprous solution. The liquid is then diluted to 50 cu cm. If a few cubic centimetres of this reagent are placed in a test tube and acetylene bubbled through, a beautiful brownish-red precipitate of copper acetylide is at once obtained.

Acetylene may be generated by the action of water on calcium carbide, the equation being



A convenient form of generating apparatus is shown in fig 22. It consists simply of an ordinary pump flask, the bottom of which has been pushed in to form a cone. The mouth of the flask is closed by a rubber stopper, through which passes a wide glass tube. Sufficient water is first put in the vessel to cover the end of the glass tube. Small pieces of carbide are now dropped in through the wide tube, and these, owing to the shape of the bottom, glide down to the edge, so that the gas bubbles generated do not escape through the glass tube.

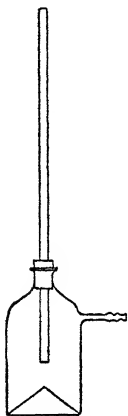


Fig 22

The presence of acetylene in coal gas may readily be demonstrated by the use of the reagent described above. A few cubic centimetres are placed in a tall cylinder provided with a glass stopper, and the air in the vessel displaced by coal gas. On shaking the reagent vigorously with the gas in the stoppered cylinder, a fine red precipitate is immediately obtained.

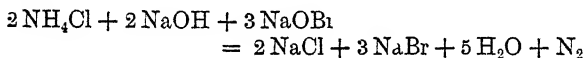
Silver test—A few cubic centimetres of silver nitrate solution are placed in a test tube, and dilute ammonia added in drops until the precipitate which first forms just redissolves. If acetylene be passed through this reagent, a white precipitate of silver acetylide is at once obtained, which soon darkens in colour. This darkening is due to the fact that acetylene obtained by the action of water on calcium carbide generally contains traces of phosphoretted hydrogen, which gives a black phosphide of silver with silver solutions. Pure acetylene gives a white precipitate with silver solutions, a dark precipitate indicates the presence of phosphoretted hydrogen, provided care has been taken to remove all sulphuretted hydrogen from the gas in question.

PART II

Volumetric Gas Analysis

Ex. 34.—Analysis of ammonium salts in the *Knop-Wagner* azotometer.

If excess of an alkaline solution of sodium hypobromite be allowed to act on an ammonium salt, the whole of the nitrogen contained in the latter is liberated as elementary nitrogen. The reaction is represented by the equation.



By measuring the volume of nitrogen liberated, the amount of ammonium salt originally present can be calculated. The reaction is readily carried out in the *Knop-Wagner* azotometer. This apparatus (fig 23) consists of a reaction or decomposition vessel A, a gas-measuring tube B, a levelling tube C, and a levelling bottle D. The decomposition vessel consists of a wide-mouthed bottle *a*, to the bottom of which is fused a small beaker *b*. The bottle is closed by a rubber stopper, through which passes a short length of glass tube provided with an ordinary glass tap. The gas-measuring tube is calibrated to 50 cu. cm., each cubic centimetre being further subdivided into $\frac{1}{5}$ cu. cm., and the tube is closed by a rubber stopper, through which passes a bent glass tube. This can be connected with the reaction vessel by the long rubber tube *d*. The levelling tube is also closed with a rubber stopper,

carrying a short bent capillary tube *e* communicating with the outside air. Attached to the bottom of the levelling tube is a bent glass tube *g*, which is connected with the levelling vessel *D* by the length of tubing *l*. The construction of the levelling vessel is readily understood from the figure. The measuring tube, levelling tube, and tube *g* are fitted into three holes in a large cork which is inserted into a tall cylinder *E*, filled with

water provided with a thermometer. Water tinted blue with indigo serves as confining liquid, and this must fill the tube *g*, rubber tubing *l*, and the length of tube below the glass tap *z* completely, so that no air is present.

As the measuring tube only holds 50 cu. cm., it is first necessary to calculate how much ammonium compound must be taken so as to obtain not more than about 45 cu. cm. of gas.

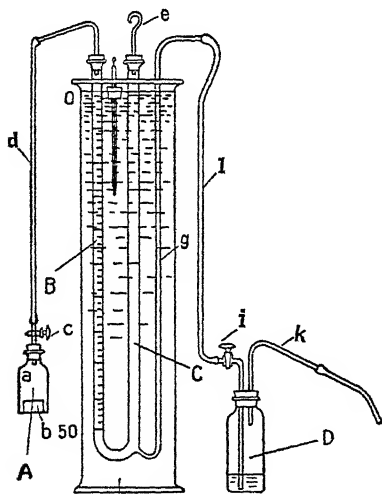


Fig 23

45 cu. cm of moist nitrogen weigh at ordinary temperature (15°) and ordinary pressure (760 mm), .05271 g. If ammonium sulphate is the compound to be analysed, then according to the equation representing the reaction 132 g. ammonium sulphate will give 28 g of nitrogen, so that the amount of ammonium sulphate which will give .05271 g will be

$$\frac{132 \times .05271}{28} = .2482 \text{ g.}$$

In making an analysis of ammonium sulphate with this apparatus, therefore, not more than 2482 g substance should be taken for each experiment.

To carry out the analysis rather less than 1 g of ammonium sulphate is weighed out accurately into a 100-cu.-cm measuring flask, dissolved in distilled water, and the solution made up to the mark

25 cu. cm of this solution are then pipetted into the *outer* vessel of the reaction vessel, and about 25 cu cm of hypobromite solution poured into the beaker

(In all similar decompositions it is important to remember that the substance to be analysed must always be placed in the outer vessel, and the reagent in the inner vessel.) The tap *c* is then removed from its socket, and after replacing the rubber stopper in the reaction vessel as tightly as possible, the vessel is immersed in a bath of water at room temperature for 5 to 10 min. In the meantime the liquid in the measuring tube must be adjusted to zero. To do this the tap *i* is opened, and the levelling bottle raised until the height of the liquid is just above the zero mark, when the tap *i* is closed and the levelling bottle placed on the table. The tap is then very cautiously opened until the lower edge of the meniscus just touches the zero mark. After inserting the tap *c* in its socket, the reaction vessel is allowed to remain a further 5 min in the water at room temperature, and it is then noted whether the height of the liquid in the measuring tube remains the same. If this is not the case, then the temperature equilibrium has not been reached, and the liquid must be again adjusted to zero and a further 5 min waited. The tap *c* is then turned so as to put the reaction vessel in communication with the measuring tube. In order that the pressure in the apparatus shall not rise unduly when the reaction starts, about 40 cu. cm. of liquid is run out

of the measuring tube by opening tap *i*. The reaction vessel is now held by the neck, and by inclining and shaking, a portion of the hypobromite is brought into the outer chamber. Nitrogen is at once evolved, and the addition of the hypobromite is slowly continued, so as to keep up a steady evolution until both liquids are mixed. The vessel is then shaken violently for about a minute, *c* closed, and the vessel again well shaken. If the column of liquid sinks when *c* is reopened the gas evolution is not quite ended, and the shaking must be continued until the level of the liquid remains constant.

The rubber stopper must be firmly inserted, so that no displacement during an analysis is possible. If this should occur, the volume of the vessel is altered, and the result thereby affected.

The vessel should be held by the neck, so as to avoid warming it with the hands.

In all gasvolumetric determinations it is necessary to shake the reacting liquids very vigorously, as otherwise supersaturation of the solution with gas readily takes place, and too low results are obtained.

The reaction flask is now cooled to room temperature by immersing for 5 to 10 min. in water, and then by raising the levelling bottle, the level of the liquid columns in the measuring and levelling tubes brought to the same height, and the volume read off. After the reaction is completed the contents of the bottle should still be pale yellow, showing that excess of hypobromite is present.

The whole of the analysis should be repeated twice more with the solution made up, and the mean of the three values taken. The temperature of the water jacket and the barometric pressure must then be noted.

The reaction between ammonium salts and alkaline hypobromite never proceeds entirely to the end there always remains about 2.5 per cent of the ammonium

salt undecomposed, and so a correction equal to 2.5 per cent must be added to the value found.

Example — 9864 g. of ammonium sulphate was weighed out, dissolved in water, and the solution made up to 100 cu. cm.

25 cu. cm. of this solution, containing .2466 g. ammonium sulphate, gave in three experiments

41.2 cu. cm.

41.4 "

41.2 "

Mean, 41.3 cu. cm. N at 16° C and 756 mm.

In order to calculate out, this volume of moist nitrogen must be converted into dry nitrogen at 0° and 760 mm. This is readily done from the equation

$$V_n = \frac{V \times 273(B - f)}{(273 + t) \times 760},$$

where V_n = volume at normal temperature and pressure (N.T.P.),

V = volume actually measured,

B = height of barometer,

t = temperature,

f = tension of water vapour at the temperature t

The tension of water vapour at 16° is 13.51 mm.

Substituting, then, the known values in the above equation, we get

$$V_n = \frac{41.3 \times 273(756 - 13.51)}{(273 + 16) \times 760} = 38.1 \text{ cu. cm.}$$

41.3 cu. cm. of moist nitrogen at 16° and 756 mm. are thus equal to 38.1 cu. cm. dry nitrogen at 0° and 760 mm.

If 1 l. of nitrogen at N.T.P. weighs 1.25523 g., then

$$38.1 \text{ cu. cm.} = \frac{1.25523 \times 38.1}{1000} = 0.04782 \text{ g.}$$

2466 g. ammonium sulphate thus yields 0.04782 g. N.

According to the equation representing the reaction,

28.08 g. N are yielded by 132.2 g. $(\text{NH}_4)_2\text{SO}_4$

0.4782 g N correspond, therefore, to

$$\frac{132.2 \times 0.4782}{28.08} = 2.251 \text{ g } (\text{NH}_4)_2\text{SO}_4;$$

or, calculated into percentages,

$$\frac{2.251 \times 100}{24.66} = 91.3 \text{ per cent.}$$

As, however, the decomposition of ammonium sulphate by alkaline hypobromite is not quantitative, but yields always 2.5 per cent too little nitrogen, a correction equal to 2.5 per cent on the result, in this case 2.28 per cent, must be added. Allowing for this, the sample of ammonium sulphate under investigation contains 93.58 per cent $(\text{NH}_4)_2\text{SO}_4$. The result may be shortly summarized as follows:

98.64 g ammonium sulphate weighed out, dissolved in water, and made to 100 cu. cm

25 cu. cm of this solution gave

1	41.2	cu. cm	N
2	41.4	„	N
3	41.2	„	N

Mean, 41.3 „ moist N at 16° and 756 mm.,

corresponding to 38.1 cu. cm dry N at N.T.P.

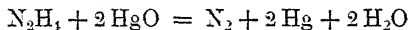
38.1 cu. cm N weigh 0.4782 g, and correspond to 2.251 g $(\text{NH}_4)_2\text{SO}_4$

The ammonium sulphate tested contains, therefore, 93.58 per cent $(\text{NH}_4)_2\text{SO}_4$, after applying a correction of 2.5 per cent

Ex. 35.—Determination of the amount of nitrogen in hydrazine salts according to *Ebler's* method.

If a hydrazine salt be mixed with an alkaline suspension of mercuric oxide, the whole of the nitrogen

contained in it will be liberated as elementary nitrogen, according to the equation:



This reaction may very conveniently be carried out by means of a Hempel gas burette, fitted with an arrangement to allow of the temperature and pressure being accurately adjusted. Such a burette may consist of a measuring tube A, holding 100 cu cm, attached by pressure tubing to the levelling vessel G, an ordinary glass tap *n* being inserted in the connecting tube (fig 24)

A *Greiner-Friederich* three-way tap is fused to the measuring tube, and this has two short capillary tubes, *a* and *b*. The capillary tube *a* is attached by a short piece of rubber tubing to a manometer F, the tubes of which are widened out at K, and each provided with a mark at exactly the same height. The manometer is completely filled up to these two marks with mercury.

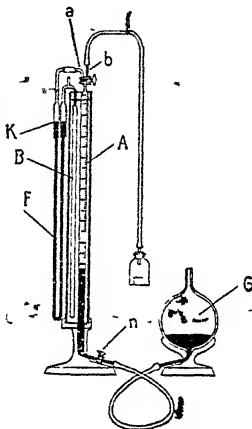


Fig 24

A compensation tube B is attached to the manometer, but for the present purpose this may be neglected.

The measuring tube and compensation tube are kept immersed in a bath of water to prevent fluctuations in temperature. The capillary tube is connected by a piece of thick-walled rubber tubing to a decomposition vessel.

Before carrying out an analysis, it is necessary to calculate how much hydrazine salt (hydrazine sulphate, N_2H_4 , H_2SO_4) must be used so as to obtain not less than 80 cu. cm. nor more than 90 cu. cm. of gas.

Four times this amount is then taken, dissolved in water and made up to 100 cu. cm., 25 cu. cm. of this solution being taken for each analysis. The height of the mercury in the measuring tube is now adjusted to any arbitrarily chosen mark, say 5, by raising the levelling vessel. 25 cu. cm. of the hydrazine sulphate solution are then placed in the outer compartment of the reaction bottle and made alkaline with 10 cu. cm. of concentrated potash solution, and 20 cu. cm. of a solution of common salt saturated with mercuric chloride placed in the inner compartment. The rubber stopper is replaced, the three-way tap loosened in its socket, and the vessel immersed in a bath of water at room temperature for 5 min. The three-way tap is now securely replaced, and turned so as to put the reaction vessel in communication with the measuring tube. The tap *n* is next opened, so that the pressure in the apparatus is considerably reduced, and by inclining the reaction vessel, the mercuric chloride solution gradually mixed with the alkaline solution of hydrazine sulphate. Yellow mercuric oxide is first precipitated, but this is then immediately reduced to black metallic mercury by the hydrazine, which is simultaneously oxidized to nitrogen and water.

During the reaction, the reaction vessel must be kept vigorously shaken. When no more gas is evolved, the reaction bottle is again immersed for 5 min. in water at room temperature. The levelling vessel is now raised, *n* being open, until the height of the mercury in it is a few millimetres above the height of the mercury in the measuring tube, and *n* is then closed. There thus exists an excess pressure in the measuring tube. The three-way tap is then turned so as to put the measuring tube in communication with the manometer *F*. This causes the mercury in the outer limb to sink, and in the inner limb to rise. By cautiously opening the tap *n*,

mercury is run out of the measuring tube until the columns of mercury of the manometer are exactly the same height. The gas in the reaction vessel is, however, also under excess pressure, so this is now put in communication with the measuring tube, and the latter again connected with the manometer and the excess pressure adjusted. This operation of connecting the reaction vessel with the measuring tube and the latter with the manometer must be continued until no displacement of the mercury columns in the manometer takes place, when the volume of gas is read off. The experiment is repeated twice more, each time with 25 cu. cm. of the hydrazine sulphate solution, and the mean of the three results taken.

The temperature and barometric pressure must now be noted.

The results are calculated out exactly in the way described in the previous exercise.

The reaction may be used not only to analyse hydrazine salts, but inversely to analyse mercury compounds by acting on them with excess of a hydrazine solution.

In this case the mercury solution must be placed in the outer, and the excess of hydrazine solution in the inner compartment of the reaction vessel.

Ex. 36.—Determination of the amount of nitric acid in nitrose by means of the *Lunge* nitrometer.

Nitric acid in presence of excess of sulphuric acid reacts with metallic mercury in such a way that the whole of the nitrogen contained in the nitric acid is liberated as nitric oxide. The reaction proceeds according to the equation.



By measuring the volume of nitric oxide evolved, the

amount of nitric acid present in a substance like nitrose can be estimated. The reaction is usually carried out in the form of nitrometer designed by *Lunge* (fig 25) The instrument consists of a gas-measuring tube and a leveling tube connected by thick-walled rubber pressure tubing. The measuring tube is graduated to 50 cu cm., each cubic centimetre being further subdivided into $\frac{1}{10}$ cu. cm, and ends in a Greiner-Friederich three-way tap,

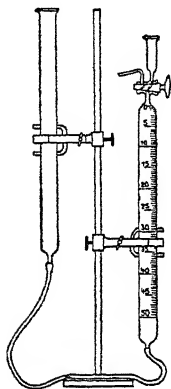


Fig 25

attached to which is a small beaker-shaped vessel. The zero point of the calibration is immediately below the tap. To use the apparatus a sufficient quantity of mercury is put in, the levelling tube is raised (after turning the tap so that the measuring tube communicates with the glass cup) until a drop of mercury appears in the little vessel, when the tap is closed. The drop of mercury is then poured out, and the levelling tube lowered until there is a considerable diminution of pressure in the measuring tube. If the tap is perfectly air-tight the mercury

will not sink, should it, however, do so, the tap must be well greased, and the operation repeated. 2 cu. cm of nitrose are now measured with a pipette, and run into the glass vessel, taking care that the liquid does not run down the sides, and drawn into the apparatus by very cautiously opening the tap. The whole of the liquid must not be drawn in, but a drop left to prevent any air getting into the bore of the stopper, or even into the tube. The small glass vessel is rinsed with 1 cu. cm. concentrated sulphuric acid, this drawn into the tube, and the vessel similarly rinsed a second time with fresh acid. The measuring tube is

then taken out of the stand, grasped firmly so that the stopper may not fall out, and brought slowly into an almost horizontal position, then suddenly returned to the vertical, taking care that the highly corrosive liquid does not come into contact with the rubber tubing. By this means the nitrose is brought into intimate contact with the mercury, and evolution of gas commences immediately. This shaking is continued for about 2 min., until no more gas appears to be evolved, and the measuring tube returned to the stand. After waiting about 5 min. to allow the temperature to fall to that of the room, the *edges* of the mercury columns in the two tubes are adjusted to the same level (the top of the meniscus being difficult to read), and the volume of gas read off. The liquid is then shaken with the mercury for about another minute, and it is observed whether the heights of the mercury columns remain the same. If not, the operation must be repeated, until the reaction is completely finished.

In taking readings in this way, i.e. adjusting the mercury columns to the same level, the gas in the measuring tube will not be under atmospheric pressure, but under a pressure smaller by the height of the acid layer. Before comparable results can be obtained, this must be compensated for by raising the level of the mercury in the levelling tube just so much as corresponds with the pressure of the column of acid. Mercury has a specific gravity of about 13, whilst that of the acid is about 2, mercury is therefore about $6\frac{1}{2}$ times as heavy as the acid. To find the height by which the mercury in the levelling tube must be raised, the height of the acid column in scale divisions must be divided by $6\frac{1}{2}$.

The mercury in the levelling tube is then raised this amount, when the gas will be under atmospheric pressure. To make sure that this is really the case, a little

sulphuric acid should be placed in the glass vessel and the tap very cautiously opened

If the pressure in the tube is greater than atmospheric pressure the acid will begin to rise, when the tap must be immediately closed and the levelling tube lowered a little. Should, however, the pressure in the tube be less than atmospheric pressure, acid will run in until the difference in pressure is equalized. When the acid which has run in has had time to collect, the volume of gas must be read off, and the temperature and barometric pressure noted. There is thus obtained the number of cubic centimetres of dry nitric oxide at known temperature and pressure which are liberated from a measured volume of nitrose, and from this data the amount by weight of nitric acid contained in 100 volumes of nitrose is readily calculated.

Example—2 cu. cm nitrose gave 31.8 cu. cm. NO at 16° and 752 mm. This volume must be reduced to N.T.P., using the equation

$$V_n = \frac{V \times 273 \times B}{(273 + t) \times 760}$$

where V_n = volume at N.T.P.,
 V = volume measured,
 B = barometric pressure,
 t = temperature

Substituting the above values, we get

$$V_n = \frac{31.8 \times 273 \times 752}{(273 + 16) \times 760} = 29.7 \text{ cu. cm. NO.}$$

As parts by weight of nitric acid are required, this volume of gas must be converted into its corresponding weight.

1 l. of NO weighs 1.3419 g. at 0° and 760 mm., so that 29.7 cu. cm. weigh

$$\frac{1.3419 \times 29.7}{1000} = .03985 \text{ g.}$$

According to the equation

30.04 g NO are equivalent to 63.05 g. HNO_3 , so that 0.3985 g. NO are equal to

$$\frac{63.05 \times 0.3985}{30.04} = 0.8365 \text{ g } \text{HNO}_3.$$

2 cu cm of nitrose contain, therefore, 0.8365 g HNO_3 , so that 100 cu cm contain

$$\frac{100 \times 0.8365}{2} = 41.8 \text{ g } \text{HNO}_3$$

The above figures may be summarized shortly as follows —

2 cu cm nitrose gave 31.8 cu cm NO (16° , 752 mm),
corresponding to 29.7 „ „ (0° , 760 „)

29.7 cu cm NO (NTP) weigh 0.4078 g, and correspond to 0.8365 g HNO_3 , so that

100 cu. cm nitrose contain 41.8 g HNO_3 .

Ex. 37.—Analysis of nitrates by means of Lunge's bulb nitrometer.

With the nitrometer used in the preceding exercise it is only possible to measure about 40 cu cm. of gas.

It is, however, often necessary to generate and measure much larger volumes of gas, particularly in the analysis of nitrates, and for this purpose Lunge has devised what is usually called a bulb nitrometer (fig. 26). This is essentially the same as the ordinary type of nitrometer, differing only in having two bulbs of capacity rather less than 100 cu cm, one on the upper part of the measuring tube, and the second on the lower part of the levelling tube. The calibration of the measuring

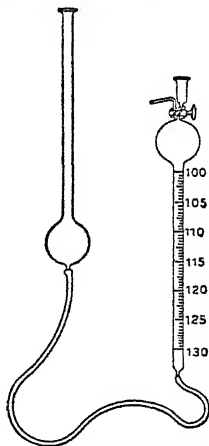
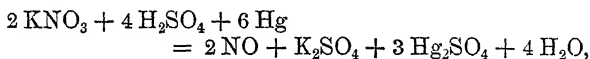


Fig. 26.—Lunge's Bulb Nitrometer

tube commences at 100 cu cm just below the bulb, and is continued to 130 cu cm

Before commencing the analysis it is necessary to calculate, from the equation



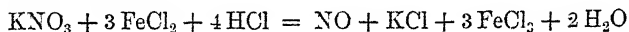
how much nitrate must be weighed out to give not less than 100 cu cm, and not more than 120 cu cm. of gas. This quantity of nitrate is then weighed out into the small glass cup, taking care that as little substance as possible adheres to the sides of the vessel. About 5 cu cm of water is then added, and when the substance has dissolved as completely as possible, the levelling tube is lowered, and the solution, together with any undissolved particles, drawn into the tube by cautiously opening the tap. The solution is rinsed into the measuring tube with two further quantities of about 5 cu cm of water. It is not advisable to use more than 15 cu. cm of water, as otherwise the sulphuric acid is diluted too much, with the result that troublesome frothing is liable to occur. About 14 to 16 cu cm. of concentrated sulphuric acid, in two lots of 7 to 8 cu. cm, are now run in, and the analysis and calculation carried out from this point exactly as described in the preceding exercise.

The Lunge nitrometer is very often used, not only for the analysis of nitric acid and its salts, but in the analysis of organic nitrates like nitroglycerine, dynamite, and gun-cotton. These are first dissolved in concentrated sulphuric acid, and the solution analysed in the nitrometer exactly as described.

Ex. 38.—Analysis of nitrates by the method of Schlosing, Grandeau, and Wagner.

This method takes advantage of the fact that if a

nitrate be added to a boiling solution of ferrous chloride, acidified with hydrochloric acid, the whole of the nitrogen in the nitrate is liberated as nitric oxide, according to the equation:



By measuring, therefore, the volume of nitric oxide obtained from a weighed amount of nitrate, the amount

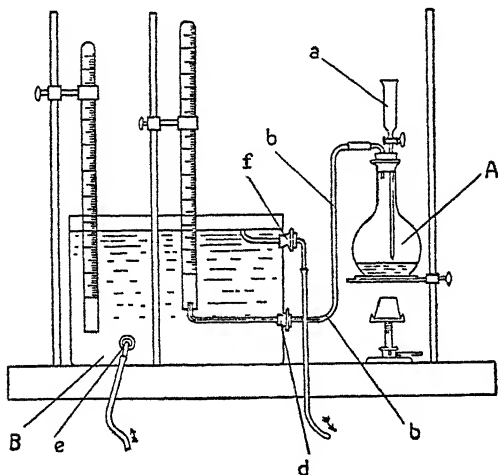


Fig 27

of pure substance in the latter may be calculated exactly as in Lunge's method

The apparatus used is shown in fig 27, and consists of a decomposition flask A and a pneumatic trough B. The decomposition flask has a capacity of about 250 to 300 cu cm, and is fitted with a two-hole stopper through one hole of which passes a funnel with stopcock *a*, the end of which is drawn out into a fine point, and through the other a bent glass tube *b* ending directly below the

stopper. The pneumatic trough B has three tubulures, one *f* near the top, and the other two *e* and *d* lower down and on opposite sides

The bent tube *b* passes through the tubulure *d*, whilst through the other tubulures pass tubes which enable a slow stream of water to be passed through the bath. To perform an analysis with this apparatus, 40 cu. cm of a solution of ferrous chloride containing 400 g FeCl_2 per litre are placed in the flask, and 40 cu cm of 20-per-cent hydrochloric acid added. A few cubic centimetres of the same acid are placed in the funnel, and the bore of the tap and glass tube filled with this by cautiously opening the tap. The point of the funnel stem should not touch the surface of the liquid, but should be about the centre of the flask. A slow stream of water is run through the trough, and the contents of the flask boiled until all air is displaced by steam. To make sure that this is really the case, a test tube filled with water should be inverted over the end of the delivery tube, when no air bubbles must collect. When all air has been displaced, a measuring tube filled with water is inverted over the end of the delivery tube *b*, and 10 cu. cm of a solution containing a weighed amount of the nitrate to be analysed is placed in the funnel, and run drop by drop into the boiling ferrous chloride solution. The nitric oxide liberated is then carried over by the steam into the graduated tube. When almost all of the nitrate solution has been run in, 10 cu. cm of 20-per-cent hydrochloric acid are added to rinse in the remainder, and when this has run in, the rinsing process is repeated a second time. (Care must be taken in running in the solutions so that no air bubbles are entangled and carried into the flask with the liquid.)

When the whole of the nitric oxide has come over, which is shown by the fact that the bubbles of steam

condense completely, the measuring tube is removed from over the delivery tube, and hung from a stand in the pneumatic trough. After placing a second measuring tube filled with water over the end of the delivery tube, the apparatus is ready for a further experiment. The experiment is then repeated twice more with the same nitrate solution. The three measuring tubes are then brought into a tall vessel filled with water at room temperature, by means of a porcelain dish filled with water, which is slipped under the open end of the tubes whilst they are being transferred. After the tubes have remained in the tall cylinder at least 5 min, they are held by the clamps with which they were supported in the cylinder, in such a way that the water stands at the same level inside the tubes as outside. The volumes of gas in the three tubes are then read off and the mean taken. The result is calculated out exactly as in Ex. 37, only in this case the tension of aqueous vapour at the temperature at which the gas is measured must be taken into account.

As the measuring tube holds only 100 cu cm of gas, the amount of nitrate to be used must be first roughly calculated so as not to exceed this volume.

If many analyses—e.g. of Chili saltpetre—have to be undertaken, the calculation of the results can be greatly simplified by the following procedure—

33 g of pure sodium nitrate are weighed out accurately, dissolved in water, and made to 1 l. 10 cu cm of this standard solution are taken, and the volume of gas obtained measured at the temperature and pressure prevailing. 33 g of the sample to be tested are then weighed out, dissolved in water, and made to 1 l, and the amount of gas liberated from 10 cu cm of this solution also determined. If v cu cm NO are obtained from the standard nitrate solution, and v_1 cu. cm. from

the sample of nitre tested, the percentage of pure sodium nitrate in the latter will be given by

$$\frac{v_1}{v} \times 100 \text{ per cent}$$

Ex. 39.—The use of the *Lunge* gasvolumeter in measuring moist gases.

In order to avoid the tedious necessity of reducing all

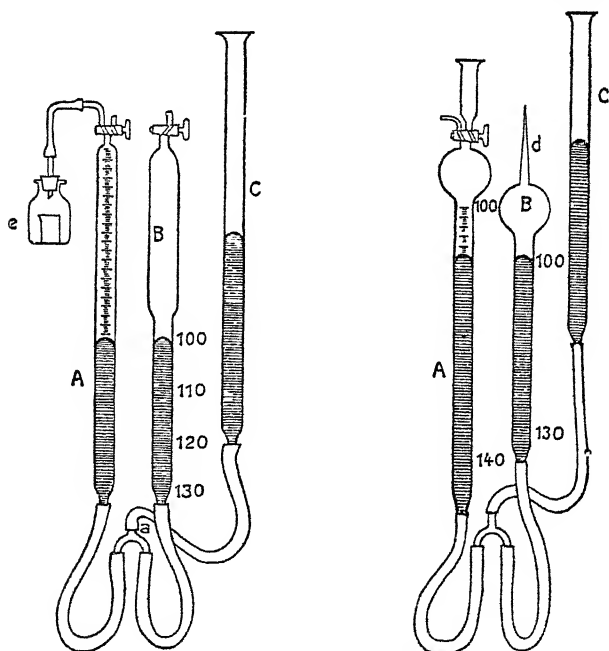


Fig 28

volumes of gases in gasvolumetric analysis to normal temperature and pressure, *Lunge* has devised an instrument which allows of the volume of the gas, reduced to N T P, to be read off directly.

The *gasvolumeter* (fig. 28), as this instrument is called,

consists of a measuring tube A, a reduction tube B, and a levelling tube C. The measuring tube is calibrated in $\frac{1}{10}$ cu. cm to 50 cu. cm, and is closed by a Greiner-Friederich stopcock, to which is sometimes attached a small glass cup. The reduction tube is widened out at the top into a bulb or cylinder, holding rather less than 100 cu. cm, and is calibrated from 100 cu. cm to 130 cu. cm, the 100 mark being just below the widened part. The tube is usually closed by an ordinary glass tap.

The three tubes are connected by thick-walled pressure tubing connected by a T piece.

The whole apparatus is mounted on an iron retort stand, in such a way that the measuring tube is held by one clamp, whilst the reduction tube and levelling tube are held by a double clamp, which allows of the tubes being raised or lowered either independently or simultaneously.

The principle upon which the apparatus depends will be clear from the following considerations. If a known volume of air be enclosed in the reduction tube, it is possible, by raising the levelling tube, to compress it so that the volume is equal to the volume it would occupy at 0° and 760 mm. This pressure will be transmitted to any gas which may be enclosed in the measuring tube, and provided that the meniscus of the mercury in the measuring tube and reduction tube is at the same height, this gas also will occupy the same volume it would occupy at 0° and 760 mm.

To adjust the apparatus for moist gases the prevailing temperature and barometric pressure are noted, and it is then calculated, from the equation

$$V_{w.f} = \frac{100 \times (273 + t) \times 760}{273(B - f)},$$

where B = barometric pressure,

t = temperature,

f = tension of aqueous vapour at t ,

what volume 100 cu cm. of moist air at 0° and 760 mm. would occupy at the temperature t and pressure B.

This volume of air is then enclosed in the reduction tube, after placing in it a drop of water to ensure that the air is saturated with aqueous vapour.

If, for example, the temperature is 18° , barometer 746 mm, and tension of aqueous vapour at 18° is 15.3 mm. mercury, these values inserted in the above equation will give

$$V_{18, 746, 15.3} = \frac{100(273 + 18)760}{273(746 - 15.3)} = 110.9,$$

i.e. 100 cu cm of moist air at 0° and 760 mm will occupy 110.9 cu cm at 18° and 746 mm.

This volume is drawn into the reduction tube by opening the tap and lowering the levelling tube, making the final adjustment with the heights of the mercury in levelling tube and reduction tube the same.

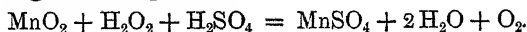
If dry gases are to be measured the method of procedure is the same, only that a drop of concentrated sulphuric acid instead of water must be placed in the reduction tube, and the volume must be calculated from the equation:

$$V_{tB} = \frac{100(273 + t)760}{273 \times B}.$$

An example of the use of the gasvolumeter is given in the following exercise.

Ex. 40.—Determination of the amount of manganese dioxide in pyrolusite, using the Lunge gasvolumeter.

If hydrogen peroxide in excess be added to manganese dioxide in presence of sulphuric acid, oxygen is evolved equivalent to the amount of manganese dioxide present, according to the equation:



The amount of manganese dioxide present in pyrolusite may be obtained by measuring the volume of oxygen obtained from a known weight of substance. To carry out the analysis, a hanging reaction bottle similar to that described in Ex 34 is attached to the side tube of the three-way tap. The sample of pyrolusite to be tested is exceedingly finely powdered, and about 17 to 19 g weighed into the outer vessel, care being taken that none of the substance falls into the inner vessel. About 5 cu. cm. of dilute sulphuric acid are next added, so that any carbonate present may be decomposed. After waiting about 5 min to allow any liberated carbon dioxide to escape, about 20 cu. cm of a 3-per-cent aqueous solution of hydrogen peroxide are run into the inner vessel, the stopper replaced, and the bottle immersed in a bath of water at room temperature for about 5 min, the glass tap being meantime loosened in its socket. When temperature equilibrium has been reached, the tap is firmly replaced in its socket, turned so as to put the measuring tube in communication with the outside air, and this then filled with mercury by raising the levelling tube. When this has been done, the tap is turned so as to connect the reaction vessel with the measuring tube. After lowering the levelling tube so as to reduce the pressure in the apparatus, the reaction vessel is gradually tilted, so that the hydrogen peroxide mixes with the pyrolusite. Oxygen is immediately evolved, the evolution being accelerated by vigorously shaking the vessel, holding it by the upper part of the neck, in order not to warm it by the hand. As the gas is liberated the levelling tube must be lowered, so that the pressure in the apparatus may not rise unduly. When the reaction is finished, the vessel must be again immersed in a bath of water at room temperature for at least 5 min. The mercury columns in the measuring tube and levelling tube are

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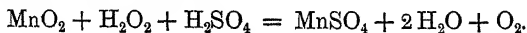
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This volume is drawn into the reduction tube by opening the tap and lowering the levelling tube, making the final adjustment with the heights of the mercury in levelling tube and reduction tube the same.

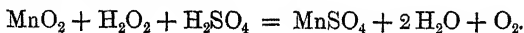
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VOLUMETRIC GAS ANALYSIS

The amount of manganese dioxide present in pyrolusite may be obtained by measuring the volume of oxygen obtained from a known weight of substance. To carry out the analysis, a hanging reaction bottle similar to that described in Ex 34 is attached to the side tube of the three-way tap. The sample of pyrolusite to be tested is exceedingly finely powdered, and about 17 to 19 g weighed into the outer vessel, care being taken that none of the substance falls into the inner vessel. About 5 cu. cm. of dilute sulphuric acid are next added, so that any carbonate present may be decomposed. After waiting about 5 min. to allow any liberated carbon dioxide to escape, about 20 cu. cm. of a 3-per-cent aqueous solution of hydrogen peroxide are run into the inner vessel, the stopper replaced, and the bottle immersed in a bath of water at room temperature for about 5 min., the glass tap being meantime loosened in its socket. When temperature equilibrium has been reached, the tap is firmly replaced in its socket, turned so as to put the measuring tube in communication with the outside air, and this then filled with mercury by raising the levelling tube. When this has been done, the tap is turned so as to connect the reaction vessel with the measuring tube. After lowering the levelling tube so as to reduce the pressure in the apparatus, the reaction vessel is gradually tilted, so that the hydrogen peroxide mixes with the pyrolusite. Oxygen is immediately evolved, the evolution being accelerated by vigorously shaking the vessel, holding it by the upper part of the neck, in order not to warm it by the hand. As the gas is liberated the levelling tube must be lowered, so that the pressure in the apparatus may not rise unduly. When the reaction is finished, the vessel must be again immersed in a bath of water at room temperature for at least 5 min. The mercury columns in the measuring tube and levelling tube are

now adjusted to the same height, and the tap of the former closed. The heights of the mercury columns in the measuring and reduction tubes must now be adjusted to the same level, and at the same time the mercury in the reduction tube must stand exactly at the mark 100. To do this, the levelling tube is raised until the mercury in the reduction tube stands exactly at the 100 mark, and then, by means of the double clamp, the reduction tube and levelling tube are simultaneously lowered until the mercury surfaces in the measuring tube and reduction tube are level. The volume of the gas in the measuring tube, now reduced to 0° and 760° mm, is then read off. The result is calculated out similarly to the analysis of ammonium salts in the Knop azotometer (Ex 34), only there is now no necessity to reduce the volume of the gas to N.T.P.

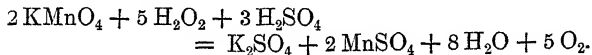
In order to obtain a satisfactory result the sample of pyrolusite must be exceedingly finely divided, otherwise a portion remains unacted upon. If, after shaking the reaction vessel for 2 min., black particles are noticeable, the experiment must be rejected. It is not permissible to shake the vessel longer than 2 min., as the insoluble portion of the pyrolusite is liable to bring about a catalytic decomposition of hydrogen peroxide into oxygen and water, in which case the result will be too high. Very hard samples of pyrolusite cannot be analysed by this method, as the decomposition is never complete. In many cases, however, it is possible to assist the reaction by warming the vessel to 70° in a bath of water, cooling finally to room temperature in a second bath.

Ex. 41.—Estimation of hydrogen peroxide, using a nitrometer with attached reaction vessel.

Hydrogen peroxide may be very conveniently estimated by taking advantage of the fact that this sub-

stance in presence of sulphuric acid reacts with a solution of potassium permanganate, liberating the whole of its active oxygen, together with an equal volume of oxygen derived from the permanganate

The reaction proceeds according to the equation:



By measuring, therefore, the volume of oxygen liberated from a known amount of a hydrogen peroxide solution when treated with excess of permanganate, the amount of pure hydrogen peroxide present may be calculated. The experiment may be conveniently carried out in a nitrometer provided with a reaction vessel (fig 29). The nitrometer differs from the ordinary pattern in having no glass cup attached, and also by having the zero mark not directly below the glass tap, but about 1 cm lower. The reaction vessel is attached by a piece of pressure tubing to the side tube of the Greiner-Friederich three-way tap, and the confining liquid used is mercury.

The hydrogen peroxide solution will require to be diluted before use. 10 cu. cm of the commercial solution containing about 3 per cent H_2O_2 is placed in a 100-cu.-cm flask, and diluted to 100 cu. cm. with distilled water. 10 cu. cm of this dilute solution are placed in the outer compartment of the reaction bottle,

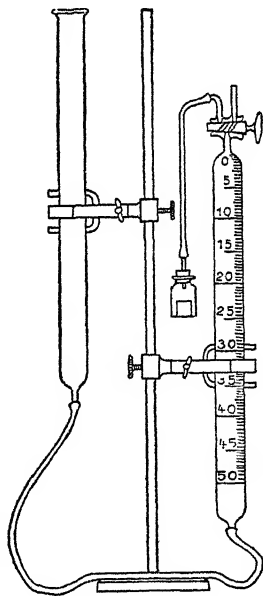


Fig 29

20 cu. cm. dilute sulphuric acid added, and 20 cu. cm. of a saturated solution of potassium permanganate placed in the inner small beaker. The vessel is now attached to the nitrometer, and immersed in a bath of water at room temperature for at least 5 min. with the stopper loose in its socket. The mercury in the levelling tube is then adjusted to the zero mark by raising the levelling tube, the stopper firmly replaced, and turned so as to put the reaction vessel in communication with the measuring tube. It is again necessary to wait a further 5 min. to see if the mercury remains at the zero mark. If it does, it shows that the temperature is constant, if not, the mercury must be again adjusted to zero, and a further period waited. Then the levelling tube is lowered to reduce the pressure in the apparatus, and the permanganate slowly mixed with the hydrogen peroxide, the reaction vessel being then thoroughly shaken until no more gas is evolved.

As the gas comes over, the levelling tube should be correspondingly lowered, so that the pressure in the apparatus does not rise to any extent.

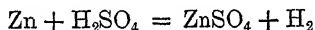
When the reaction is complete the solution should still be coloured by the permanganate, showing that excess is present. If the solution be colourless, too little permanganate has been taken, and the experiment must be rejected. Before reading off the volume of gas liberated, the reaction vessel must be cooled for at least 5 min. in water to room temperature. The temperature and barometric pressure must then be read, and the results obtained calculated, as in Ex. 34.

Just as a solution of hydrogen peroxide may be estimated by using excess of potassium permanganate, so it is possible, on the other hand, to analyse a solution of a permanganate, using excess of hydrogen peroxide. This method may very conveniently be used to standardize

the solutions of potassium permanganate used in volumetric analysis, the results obtained being at least as accurate as when iron or oxalic acid is used for the purpose

Ex. 42.—Valuation of zinc dust according to the method of *Franz Meyer*.

Zinc dust, which is obtained as a by-product in the manufacture of zinc, consists principally of metallic zinc, with varying amounts of zinc oxide. It also usually contains small amounts of iron, lead, cadmium, &c. Zinc dust is a very energetic reducing agent, and as such finds extensive application in the chemical industry, its value for this purpose entirely depending on the amount of hydrogen which it is able to evolve. The method of *Franz Meyer* for the valuation of zinc dust consists of measuring the volume of hydrogen obtained by dissolving a known weight of the substance in dilute sulphuric acid, the equation representing the reaction being



The analysis is carried out in the apparatus shown in the diagram (fig 30). It consists of the reaction flask A, the tap-piece B, and the measuring tube D. The measuring tube and reaction flask are connected to the tap-piece by ground-in joints. The measuring tube is widened out at the top into a bulb of 260 cu cm. capacity, and the graduation is continued down the narrow tube to 460 cu cm, each cubic centimetre being further subdivided into $\frac{1}{2}$ cu. cm. The bulb of the measuring tube ends in a capillary closed by the simple glass tap E. The tap-piece B has a three-way tap C, the construction of which is best understood from the figure. The tube of the tap is connected by a long piece of pressure tubing, preferably provided with a pinchcock, to the levelling

bottle F, which has a capacity of about 500 cu cm. The capacity of the measuring tube is so chosen that, working at ordinary temperatures (10–25°) and ordinary pressures (740–770 mm), 1 g of zinc dust containing 75–100 per

cent of metal may be taken for an analysis.

The joints and taps are first well greased, and then about 1 g. zinc dust weighed into the reaction flask. The levelling bottle is then filled with distilled water, the tap C turned into position I, and the reaction flask completely filled with water by raising the levelling bottle and opening the pinchcock. When all air has been displaced C is turned into position II, the water emptied out of the levelling bottle and replaced by dilute sulphuric acid ($1 \text{ H}_2\text{SO}_4 : 3 \text{ H}_2\text{O}$). The

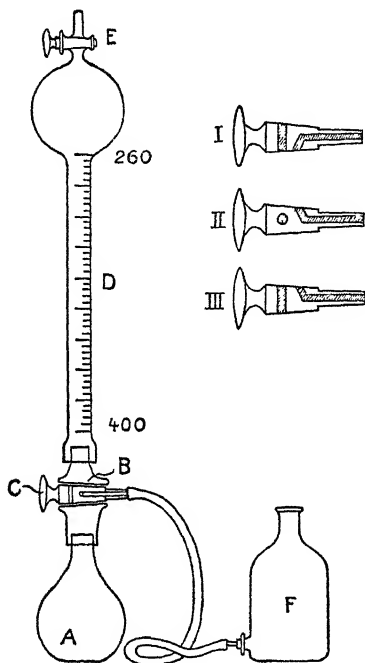


Fig 30

air in the measuring tube is then displaced by dilute acid by raising F, and then tap E closed. The pinchcock is now removed, and the tap C turned into position III. The denser acid sinks down, mixes with the water in the reaction flask, and the evolution of hydrogen begins. When the whole of the zinc has dissolved, the surface of the liquid in the levelling flask is brought to the same level as the liquid in the measuring tube, and the

volume of hydrogen read off. The temperature and barometric pressure is then noted, and the volume reduced to dry gas at 0° and 760 mm.

From the equation the amount of metallic zinc present in the zinc dust is then readily calculated.

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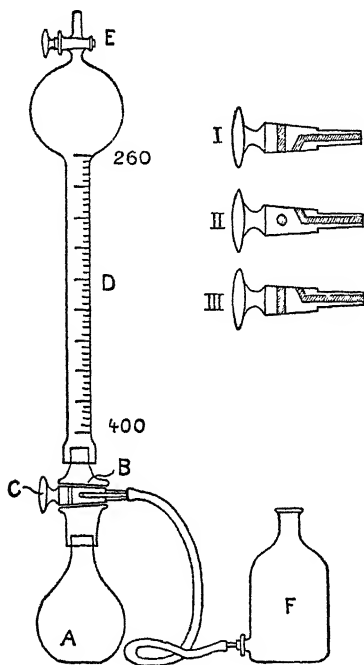


Fig 30

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From the equation the amount of metallic zinc present in the zinc dust is then readily calculated.

APPENDIX

TENSION OF AQUEOUS VAPOUR ACCORDING TO REGNAULT

In Millimetres Mercury

Temperature	Tension	Temperature	Tension
5 0°	6 534	15 5°	13 112
5 5°	6 736	16 0°	13 536
6 0°	6 998	16 5°	13 972
6 5°	7 242	17 0°	14 421
7 0°	7 492	17 5°	14 882
7 5°	7 751	18 0°	15 357
8 0°	8 017	18 5°	15 845
8 5°	8 291	19 0°	16 346
9 0°	8 574	19 5°	16 861
9 5°	8 865	20 0°	17 391
10 0°	9 165	20 5°	17 935
10 5°	9 474	21 0°	18 495
11 0°	9 792	21 5°	19 069
11 5°	10 120	22 0°	19 659
12 0°	10 457	22 5°	20 265
12 5°	10 804	23 0°	20 888
13 0°	11 162	23 5°	21 528
13 5°	11 530	24 0°	22 184
14 0°	11 908	24 5°	22 858
14 5°	12 298	25 0°	23 550
15 0°	12 699		

WEIGHT OF 1 L OF VARIOUS DRY GASES

At 0° C and 760 mm.

Hydrogen	0.08988 g
Oxygen	1.42923 "
Nitrogen	1.2505 "
Nitric oxide	1.3412 "

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